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GEOMETRICAL INVERSION IN THE ACIDS DERIVED FROM THE COUMARINS.

Part II.* *Cis* To *Trans*.

By T. R. Seshadri
and
P. Suryaprakasa Rao.
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Received January 29, 1936.

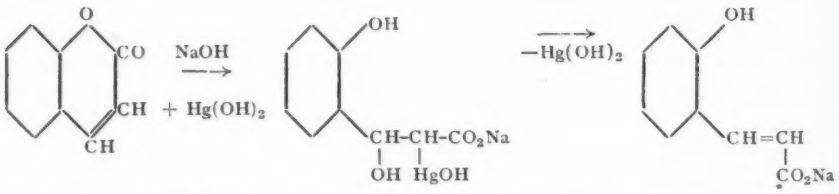
In discussing the mechanism of geometrical inversion in the acids derived from the coumarins (Seshadri, 1934) it was pointed out that *cis* to *trans* inversion takes place in an alkaline medium in which coumarins first form alkali salts of coumarinic acids and that addition of some addenda at the double bond is a requisite preliminary to the final inversion to the coumaric acids. In that connection mention was made that the results of the action of mercury compounds on coumarins (Sen and Chakravarti, 1929 and 1930) could be explained as due to the influence of substituent groups present in the benzene or pyrone ring. With a group of coumarins as exemplified by 6-nitro- and 6 : 8-dibromocoumarins they obtained coumaric acids whereas with others which contained alkyl and hydroxyl groups they obtained mercurated compounds.

According to the above-mentioned mechanism coumarin itself should give rise to coumaric acid or mercurated coumaric acid. By the action of sodium hydroxide and mercuric acetate in the cold Sen and Chakravarti (*loc. cit.*) reported the isolation of a diacetoxy-mercuri-coumaric acid where as Naik and Patel (1934), using apparently the same method, claimed to have obtained 6 : 8-bisacetoxy-mercuri-coumarin. By boiling, however, an alkaline solution of coumarin with mercuric oxide, the former authors stated, that they obtained mercurated coumarins. The reaction of alkali and mercuric acetate has now been investigated by us following Sen and Chakravarti's procedure and the product is found to be as they claimed a mercurated coumaric acid and not a mercurated coumarin (*cf.* Naik and Patel). By the mercuric oxide method of the same authors was obtained a compound which they believed to be 6-chloromercuri-coumarin and which is now found to be also a mercurated coumaric acid. It dissolves in aqueous sodium carbonate and bicarbonate and yields coumaric acid readily when hydrogen

* Part I of this series was published in *J. I. C. S.*, 1934, 743-49.

sulphide is passed into an alkaline solution of the compound in order to precipitate the mercury and subsequently the filtered solution is acidified. In the presence of cold caustic alkali and yellow mercuric oxide coumarin undergoes transformation into coumaric acid so easily that this inversion could not have failed to take place under the conditions mentioned above. Based upon this observation a very rapid and cheap method has been worked out for the preparation of pure coumaric acid from coumarin. 7-methylcoumarin behaves similarly and gives rise to a good yield of 4-methylcoumaric acid whereas 6-nitrocoumarin is unaffected in the cold even after treatment for several hours. Only the unstable nitro-coumarinic acid is produced which rapidly reverts to the nitrocoumarin. But at the boiling point the inversion takes place fairly easily giving rise to a good yield of 5-nitrocoumaric acid. Under these vigorous conditions coumarin and methylcoumarin undergo mercuration besides inversion and so produce mercurated coumaric acids.

The part played by mercuric oxide in effecting the inversion may be represented as below:



It adds on to the double bond in the *cis* stage and after the required rotation of the groups has taken place gets eliminated from the *trans* stage. In support of this may be mentioned (1) observations in which *cis* compounds add on mercury compounds readily whereas the corresponding *trans* compounds do not react or do so only slowly under the same conditions (Biilmann, 1912; Wright, 1935) and (2) the easy decomposition in the presence of alkali of addition compounds like methoxymelilotic acid and sodium dihydrocoumaric acid-β-sulphonate to give coumaric acid. The greater difficulty with which *trans* inversion takes place with 6-nitrocoumarin by the present method agrees with previous experience using other methods (Dey and Row, 1924; Dey, Rao and Seshadri, 1934). This may be attributed to the nature of the nitrogroup as an electron sink which diminishes the tendency to undergo inversion.

Experimental.

Preparation of O-coumaric acid.—Finely powdered coumarin (8 g.) was treated with cold aqueous caustic soda (8 g. in 100 c.c.), yellow mercuric

oxide (1 g.) added and the mixture shaken vigorously for ten minutes. Coumarin dissolved rapidly and the solution assumed a light yellow colour with a green fluorescence. It was then filtered through an ordinary filter without suction, the residue washed twice with small quantities of water and the collected filtrate acidified with concentrated hydrochloric acid. The colourless crystalline precipitate that was obtained was filtered at the pump and washed with small quantities of water. The yield was almost theoretical and the acid was pure melting at 208–10° (decomp.). When tested by passing hydrogen sulphide into an alkaline solution of the acid it gave no precipitate of mercuric sulphide thereby showing that it was free from mercury. Care should be taken that no rise of temperature takes place as otherwise some mercuration is effected.

4-*Methylcoumaric acid* was prepared from 7-Methylcoumarin (5 g.) by closely following the above procedure. The yield of the pure acid melting at 195–6° was 5 grams.

5-*Nitrocoumaric acid* could not be obtained by treatment in the cold as above. Only the unstable coumarinic acid was formed which reverted rapidly into the original nitrocoumarin. It was therefore made by following the method of Sen and Chakravarti (1930). The following modification of their method was found to give better yields. After boiling 6-nitrocoumarin in alkaline solution with mercuric oxide the crude nitrocoumaric acid was precipitated with hydrochloric acid and then purified by treatment with sodium bicarbonate instead of ammonia and by subsequent precipitation of the pure acid. This minimised contamination with unchanged nitrocoumarin which dissolved to a considerable extent in ammonia and only sparingly in sodium bicarbonate. Yield of the pure acid after crystallisation from alcohol was 4·5 grams from 5 grams of the nitrocoumarin.

Action of sodium hydroxide and mercuric acetate on coumarin.—By following the procedure of Sen and Chakravarti a compound (diacetoxymercuricoumaric acid) was obtained which exhibited all the properties and reactions mentioned by them. It dissolved easily in cold aqueous sodium carbonate and bicarbonate and was therefore a diacetoxymercuri-coumaric acid and not a coumarin.

For obtaining pure coumaric acid from it the method of Sen and Chakravarti—boiling with dilute hydrochloric acid—was not found to be suitable. Removal of mercury was not always complete so that the product frequently melted low. A convenient method is to dissolve the mercurated compound in dilute ammonia and pass hydrogen sulphide till the precipitation of mercury sulphide is complete. It is then filtered and the clear filtrate acidified with

hydrochloric acid. The crystalline precipitate melts with decomposition at 208-210° when filtered and washed with water and is found to be pure coumaric acid.

Action of hot sodium hydroxide and mercuric oxide on coumarin.—The product that was considered by Sen and Chakravarti to be 6-chloromercuricoumarin was prepared by their method (1929, p. 851). It was a colourless partly crystalline powder melting with decomposition at about 180° and was found to be soluble in aqueous sodium carbonate and sodium bicarbonate with evolution of carbon dioxide. Pure coumaric acid was obtained easily from it by the hydrogen sulphide method described above. It was therefore a mercurated coumaric acid and not a coumarin. It should be mentioned that these mercuration products underwent marked change when preserved over long periods and their solubility in aqueous sodium carbonate diminished.

Summary.

A rapid and efficient method has been found for preparing coumaric acid and 4-methylcoumaric acid from coumarin and 7-methylcoumarin respectively by treatment with mercuric oxide in the presence of cold alkali. 5-nitrocoumaric acid is not produced in the cold and is formed only by boiling the mixture of 6 nitrocoumarin, mercuric oxide and alkali. The action of cold alkali and mercuric acetate or of hot alkali and mercuric oxide on coumarin yields mercurated coumaric acids. From these pure coumaric acid can be produced by using ammonia and hydrogen sulphide.

REFERENCES.

1. E. Biilmann, *Annalen*, 1912, **388**, 259.
2. B. B. Dey and K. K. Row, *J. C. S.*, 1924, 555.
3. B. B. Dey and R. H. Row and T. R. Seshadri, *J. I. C. S.*, 1934, 743.
4. K. G. Naik and A. D. Patel, *J. C. S.*, 1934, 1043.
5. R. N. Sen and D. Chakravarti, *J. I. C. S.*, 1929, 849; 1930, 247.
6. T. R. Seshadri, *J. C. S.*, 1928, 166; *Current Science*, 1934, **3**, p. 19.
7. G. F. Wright, *J. A. C. S.*, 1935, 1993.

ULTRASONIC VELOCITIES IN LIQUID MIXTURES.

By S. Parthasarathy.

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Received March 12, 1936.

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction.

In an earlier paper[1] the author gave experimental determinations of ultrasonic velocities in a number of organic liquids by the method of diffraction of light by sound waves of high frequency. The present paper deals with ultrasonic velocities in mixtures of organic liquids by the same experimental method, as such information will be valuable for calculating the compressibilities of liquid mixtures.

The experimental arrangement is the one followed in earlier investigations, and it has been described in full.

All the usual precautions which may vitiate the results have been duly taken and since they have been fully discussed already, we shall not repeat them here.

The liquids used were of the purest stock, used after distillation. The densities of the pure liquids and of the mixtures were determined by a specific gravity bottle. For mixtures, as soon as the additional quantity of the second component was added to the first component contained in a stoppered conical flask, the mixture was thoroughly shaken, and the density determined in the usual way. The concentrations were found out from the weights of the second component added, from time to time.

All the experiments were carried out at 23° C. which was the temperature maintained in the room. The frequency employed was $7 \cdot 37 \times 10^6$ cycles per second.

2. Results.

Four binary liquid mixtures of,

(1) Benzene and carbon tetrachloride ;
(2) Carbon disulphide and carbon tetrachloride ;
(3) Ethyl acetate and carbon tetrachloride ; and
(4) Tetralin and carbon tetrachloride

have been studied for ultrasonic velocities at various concentrations. Incidentally, the adiabatic compressibilities were also calculated for the mixtures.

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[1] S. Parthasarathy, *Proc. Ind. Acad. Sci.*, 1935, **2**, 497.

The results of investigations in these four liquid mixtures are given in four tables. Column five contains experimental results of ultrasonic velocities, column three the densities and column six the adiabatic compressibilities calculated therefrom.

TABLE I.

(*a*) *Mixture of Benzene and Carbon Tetrachloride; at 23°C.*

	Benzene % by weight	CCl_4 % by weight	Density	Wave-length of sound in mms.	Velocity of sound in meters/sec.	Adiabatic compressibility $\beta\phi \times 10^6$
1	100	..	0·8725	0·1780	1312	66·4
2	72·1	27·9	1·001	0·1629	1201	69·2
3	56·6	43·4	1·086	0·1545	1139	71·0
4	35·2	64·8	1·237	0·1422	1048	73·5
5	23·0	77·0	1·340	0·1381	1018	72·0
6	..	100	1·596	0·1258	927·2	72·9

TABLE II.

(*b*) *Mixture of Carbon Disulphide and Carbon Tetrachloride; at 23° C.*

	CS_2 % by weight	CCl_4 % by weight	Density	Wave-length of sound in mms.	Velocity of sound in m./s.	Adiabatic compressibility $\beta\phi \times 10^6$
1	100	..	1·258	0·1560	1150	60·1
2	73·1	26·9	1·331	0·1479	1090	63·3
3	58·1	41·9	1·374	0·1423	1049	66·2
4	39·2	60·8	1·436	0·1373	1012	68·1
5	20·0	80·0	1·502	0·1320	972·7	70·4
6	..	100	1·596	0·1258	927·2	72·9

TABLE III.

(*c*) *Mixture of Ethyl Acetate and Carbon Tetrachloride; at 23° C.*

	Ethyl acetate % by weight	CCl_4 % by weight	Density	Wave-length of sound in mms.	Velocity of sound in m./s.	Adiabatic compressibility $\beta\phi \times 10^6$
1	100	..	0·8989	0·1605	1184	79·3
2	69·6	30·4	1·034	0·1517	1119	77·3
3	40·9	59·1	1·200	0·1425	1051	75·5
4	25·1	74·9	1·313	0·1361	1003	75·7
5	16·4	83·6	1·404	0·1336	984·2	73·5
6	..	100	1·596	0·1258	927·2	72·9

TABLE IV.

(*d*) *Mixture of Tetralin and Carbon Tetrachloride*; *at* 23° *C.*

	Tetralin % by weight	CCl_4 % by weight	Density	Wave-length of sound in mms.	Velocity of sound in m./s.	Adiabatic compressibility $\beta\phi \times 10^6$
1	100	..	0·9681	0·1991	1468	48·0
2	67·3	32·7	1·125	0·1766	1301	52·5
3	45·6	54·4	1·240	0·1618	1192	56·7
4	28·8	71·2	1·348	0·1499	1105	60·8
5	18·1	81·9	1·424	0·1406	1036	65·1
6	..	100	1·596	0·1258	927·6	72·9

The three graphs, Fig. 1, Fig. 2 and Fig. 3, give the relation between (1) the concentration and the density, (2) the concentration and the ultrasonic

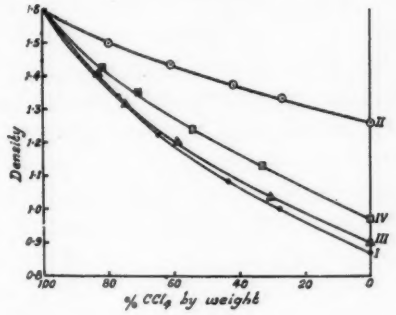

FIG. 1.

velocity, and (3) the concentration and the adiabatic compressibilities of the mixtures. Along the concentration axis, only the weight percentage of carbon tetrachloride is mentioned, as this liquid is common to all, while the percentage of the second component can be easily obtained by simple difference. The curves are all numbered corresponding to the mixtures as given in the tables.

3. *Discussion.*

So far no direct determinations have been made of sound velocities in liquid mixtures. The method of diffraction of light by high frequency sound waves offers an easy and quick method for determining sound velocities and adiabatic compressibilities and this method has been applied to four liquid mixtures.

Fig.2 shows that for mixtures (1) carbon tetrachloride and benzene, and (2) carbon disulphide and carbon tetrachloride, the relation between con-

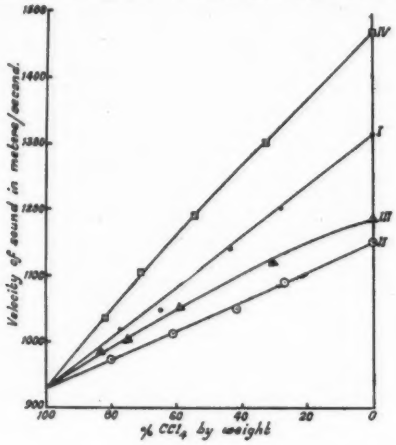

FIG. 2.

centration and sound velocity is strictly linear; while for the other two mixtures, the graphs are slightly concave towards the concentration axis, being much less so for tetralin and carbon tetrachloride, the mixture (4).

Fig. 3 shows that the graphs for the mixtures (*a*) CCl_4 and CS_2 and (*b*) CCl_4 and ethyl acetate are straight lines depicting strict linearity of adiabatic compressibility with concentration. That for benzene and CCl_4 is concave

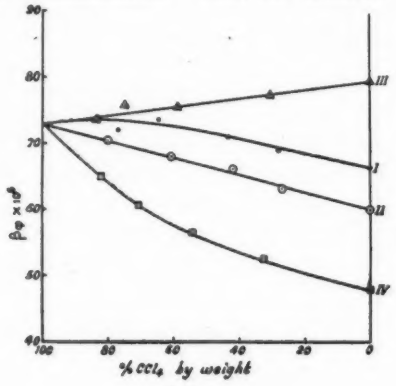

FIG. 3.

while the graph for CCl_4 and tetralin is convex towards the concentration axis.

These are explicable if we study the relationship between the density and concentration of these mixtures. For then here, the adiabatic compressibility has been calculated from both sound velocity and density, and is not a direct and separate determination.

From these results one can say that the sound velocities vary almost linearly with the concentration in the case of mixtures.

In this connection, we may remark that when the author was studying[2] the light-scattering in liquid mixtures, he observed some anomalies. On plotting the concentration θ_1 of the mixture against the intensity of scattered light I, the author found that there were three typical kinds of curves:

(1) the curve being concave towards the θ_1 axis; as in benzene and CCl_4;

(2) the graph being a straight line; as in ethyl acetate and CCl_4; and

(3) the curve being convex towards θ_1 axis; as in CCl_4 and nitrobenzene, and CCl_4 and CS_2.

We shall now compare the forms of curves in the two cases: (1) of intensity of scattered light to concentration of the earlier paper, and (2) the adiabatic compressibility with concentration contained in this paper. Of the four mixtures studied, three have been experimented on in both the papers.

(*a*) *Benzene and carbon tetrachloride.*—The curve, the intensity of scattered light with concentration, has a form concave to the latter axis; that is for intermediate positions, the intensity is greater. The adiabatic compressibility-concentration curve is also of the same form; the compressibility is greater at intermediate concentrations. This is naturally to be expected as an increase in compressibility gives an increase in the intensity of scattered light.

(*b*) *Carbon disulphide and carbon tetrachloride.*—The graph for this mixture in the light-scattering studies, takes an opposite shape to the case under (*a*), being very slightly convex towards the concentration axis. The course of the curve in compressibility-concentration is almost a straight line. But it must be remarked here that the changes observed are not great.

(*c*) *Ethyl acetate and carbon tetrachloride.*—The graph was observed to be a straight line in the light-scattering studies, the relation between I and θ_1 being strictly proportional. Here also, the relation between the adiabatic

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[2] S. Parthasarathy, *Ind. Jour. Phys.*, 1934, **7**, 275.

compressibility and concentration is linear, which explains the result in the earlier paper.

The mixtures studied in the light-scattering work were completely miscible and it is well known that in such cases, where one does not work near the critical solution temperature, the intensity of concentration-scattering is negligible compared to density and orientiation scattering, which density scattering involves the compressibility. This is clear from the calculations shown in the author's paper on light-scattering on page 307. Hence we are justified in observing the changes in the curves as mainly due, if not wholly, to the compressibility not varying linearly with concentration.

It may be remarked here that this method of getting the values for the compressibilities of binary liquid mixtures has been useful in explaining some of the anomalies observed earlier, which otherwise would not have been possible.

It is known that in all the expressions for the intensity of scattered light, we are concerned with the isothermal compressibility β_T and not with β_ϕ. These two compressibilities are related together and is given by the expression :

$$\beta_T = \beta_\phi + \frac{\alpha^2 T}{JC_p d}$$

where α is the coefficient of thermal expansion,

C_p is the specific heat at constant pressure at absolute temperature T,

J is the mechanical equivalent of heat, and

d is the density

so that any variation in β_ϕ will also affect β_T. In the expression on the right-hand side β_ϕ is large compared to the second term, and unless there are large variations in α and d, we can, without error, say that the course of the curves for both β_T and β_ϕ will be similar. Hence, we are not wrong in applying, at least qualitatively, the results of β_ϕ in mixtures to light-scattering experiments.

Since, in the formula given above, necessary data regarding α and C_p are lacking for the mixtures at different concentrations, we cannot fully work out the values for β_T for all these mixtures.

The author thanks Sir C. V. Raman, Kt., for the interest shown in this work.

Summary.

The paper gives results and graphs of (*a*) ultrasonic velocities and (*b*) adiabatic compressibilities in the following four binary liquid mixtures in all of which one component is carbon tetrachloride ; the second component being (1) benzene, (2) carbon disulphide, (3) ethyl acetate and (4) tetralin.

The variation of adiabatic compressibility of the mixture was found to be not always strictly proportional to concentration. These results are applied to experimental investigations in an earlier paper of the author[2] where it was observed that the intensity of scattered light in binary liquid mixtures (completely miscible and at temperatures far removed from the critical solution temperature) was not always proportional to concentration. The trend of the curve in light-scattering and compressibility studies is the same, being concave or convex towards the concentration axis in both the cases, or being straight. The agreement is satisfactory.

ON A FUNCTION CONNECTED WITH THE SINGULAR SERIES.

By K. Sambasiva Rao.

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(Communicated by Dr. S. Chowla.)

Notation.

$$(1) \quad s_\zeta = \sum_{h=0}^{q-1} \zeta^{h^n}$$

where, for integers $(a, q) = 1$, $\zeta = e^{2\pi i \frac{a}{q}}$ is a primitive qth root of unity and n is an integer $\geqslant 2$.

$$(2) \quad A_{n,s}(q, N) = q^{-s} \sum_{\zeta} (s_\zeta)^s \zeta^{-N}$$

where the summation extends over all primitive qth roots, of unity, and N is an integer.

$$S = \sum_{q=0}^{\infty} A(q)$$

is known as the singular series. Also, it is known* that

$$S = \prod_{p} \chi_p$$

where p runs through all primes and

$$\chi_p = \sum_{l=0}^{\infty} A(p^l).$$

$M(p^l, N)$ denotes the number of solutions of $\sum_{\nu=1}^{s} h_\nu^n \equiv N \pmod{p^l}$, where $0 \leqslant h_\nu < p^l$.

$p^\theta \,//\, N$ denotes that
$p^\theta \,|\, N$ but $p^{\theta+1} \nmid N$.

It is known from the researches of Hardy and Littlewood that $A(p^l)$ vanishes for values of l on and after a certain stage. This is given as the

Theorem I. If $p^{\beta_n+\sigma} \,//\, N$, then

$A(p^l) = 0$ for $l > \text{Max}(\beta_{n+\sigma+1}, \beta_{n+\gamma})$ where $0 \leqslant \sigma < n$ and $\gamma = \theta + 1$ for all $p > 2$, θ being defined by $p^\theta \,//\, n$.

In the particular case when $p \nmid n$ (which is true after a certain point), this theorem becomes

* See Landau's *Vorlesungen über Zahlentheorie*, Band I, referred to, in this paper, at any subsequent time, as LVI.

THEOREM II. If $p^{\beta}n+\sigma \,//\, N$, $(p, n)=1$, then $A(p^l)=0$ for $l>\beta n+\sigma+1$.

This note contains a very simple proof of the above proposition. For this purpose the following simple lemmas are needed

Lemma 1†. For $q = p^l$, $p \nmid n$, $2 \leqslant l \leqslant n$

$$s_{\zeta} = p^{l-1}$$

Lemma 2†. For $q = p^l$, $l > n$

$$s_{\zeta} = p^{n-1}\, s_{\zeta p^n}.$$

Note :—ζp^n is a primitive $p^{(l-n)}$th root of unity.

Lemma 3. If ζ is a primitive p^lth root of unity, then

$\sum_{\zeta} \zeta^{p^r} = 0$ whenever $l > r+1$, or, in other words,

$$\sum_{\substack{0<a<p^l \\ (a,\,p^l)=1}} e^{2\pi i \frac{a}{p^m}} = 0 \qquad \text{whenever } 1 \leqslant m \leqslant l.$$

Proof :—

$$\sum_{\substack{a<p^l \\ (a,\,p^l)=1}} e^{2\pi i \frac{a}{p^m}} = p^{l-m} \sum_{\substack{a<p^m \\ (a,\,p^m)=1}} e^{2\pi i \frac{a}{p^m}}$$

Also, $e^{2\pi i \frac{a}{p^m}}$ for each $a < p^m$, $(a, p^m) = 1$, is a root of the equation

$$\frac{x^{p^m}-1}{x^{p^{m-1}}-1} = 0$$

The equation can be given as

$$x^{(p-1)\,p^{m-1}} + x^{(p-2)p^{m-1}} + \cdots + 1 = 0$$

The sum of the roots of the above equation is zero for $m > 1$, since

$$(p-1)\,p^{m-1} > (p-2)\,p^{m-1} + 1.$$

This proves the lemma.

Proof of Theorem II.

Let $l = an + r$ where $0 < r \leqslant n$.

We have by Lemma 2

$$s_{\zeta} = p^{a(n-1)}\, s_{\zeta'} \tag{A}$$

where ζ' is a primitive p^rth root of unity, and $\zeta' = e^{2\pi i \frac{a}{p^r}}$. In the case when $r \neq 1$, from (A) and lemma 1 it follows that

$$s_{\zeta} = p^{a(n-1)}\, p^{r-1}$$
$$= p^{l-(a+1)}.$$

† LVI, pp. 294 and 297.

Therefore

$$A(p^l) = p^{-ls} \times p^{ls-s(\alpha+1)} \sum_{\zeta} \zeta^{-N}$$
$$= p^{-s(\alpha+1)} \sum_{\zeta} \zeta^{-N}.$$

But

$$\text{(B)} \qquad \sum_{\zeta} \zeta^{-N} = \sum_{\substack{a < p^l \\ (a, p^l) = 1}} e^{\frac{-2\pi i a}{p^l} N_0 \cdot p^{\beta n+\sigma}}$$

Where $N = N_0 p^{\beta n+\sigma}$ and $(N_0, p) = 1$.
Also when a runs through a reduced residue system mod p^l, so does $-N_0 \times a$. Therefore,

$$\text{(C)} \qquad \sum_{\zeta} \zeta^{-N} = \sum_{\substack{b < p^l \\ (b\ p^l) = 1}} e^{\frac{2\pi i\, b}{p^l - (\beta n+\sigma)}}$$

$= 0$ by lemma 3, whenever $l > \beta n+\sigma+1$. In the case when $r = 1$, from (A) we have

$$A(p^l) = p^{-ls+s\alpha(n-1)} \times \sum_{\substack{a < p^l \\ (a, p^l) = 1}} e^{\frac{-2\pi i a N}{p^l}} \times \left(\sum_{h=0}^{p-1} e^{\frac{2\pi i a h^n}{p}} \right)^s$$

But

$$\sum_{a} e^{\frac{-2\pi i a N}{p^l}} \left(\sum_{h} e^{\frac{2\pi i a h^n}{p}} \right)^s$$
$$= \sum_{a} e^{\frac{-2\pi i a N}{p^l}} \sum_{0 \leqslant h_\nu < p} e^{2\pi i \frac{a}{p} (h_1^n + \cdots + h_s^n)}$$
$$= \sum_{a} e^{\frac{-2\pi i a N}{p^l}} \sum_{t=0}^{p-1} M(p, t)\, e^{\frac{2\pi i a t}{p}}$$
$$= \sum_{t=0}^{p-1} M(p, t) \sum_{a} e^{\frac{-2\pi i a N}{p^l}} \times e^{\frac{2\pi i a t}{p}}.$$

But

$$\sum_{\substack{a < p^l \\ (a, p^l) = 1}} e^{\frac{-2\pi i a N}{p^l}} \times e^{\frac{+2\pi i a t}{p}}$$
$$= \sum_{a} e^{\frac{2\pi i a\, p^{\beta n+\sigma}}{p^l} - N_0 + t p^{\left(l - (\beta n+\sigma+1)\right)}}$$

$= 0$ whenever $l > \beta n+\sigma+1$ for reasons similar to those given for (B) and (C). Hence the proposition is proved.

THE RAMAN SPECTRUM AND ELECTROLYTIC DISSOCIATION OF SELENIC ACID.

By C. S. Venkateswaran.

(From the Department of Physics, Indian Institute of Science, Bangalore.)

Received March 26, 1936.

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction.

In the previous communications to these *Proceedings*[1] the author has shown how a detailed study of the Raman spectra of weak acids like iodic and phosphoric acids yield information regarding the progressive electrolytic dissociation of these acids in aqueous solutions. The present paper deals with the results obtained in a similar investigation with selenic acid. The Raman spectrum of a strong solution of this acid has been studied by A. S. Ganesan[2] and he has reported five lines of frequency shifts* 315 (*m*), 422 (*m*), 730 (*f*), 850 (*s*), 926 (*f*) which differ in a marked manner from the shifts of the modified lines in selenates. A quantitative study of the Raman spectrum of this acid for a wide range of concentrations and a comparison of the results with those of sulphuric acid appear to be of great interest; for it could be expected to yield some information regarding the properties of similar compounds belonging to the same homologous series in the periodic system. The Raman spectra studies of sulphuric acid are numerous and though the results are vitiated to some extent by the presence of a strong continuous spectrum, there is general agreement among the several investigators regarding the evidence for the stepwise dissociation of this acid. In the case of selenic acid, as far as the author is aware of, there are no physico-chemical data available at present indicating its stages of ionisation. It can also be easily obtained in the crystalline form in which it exists as hundred per cent acid and it possesses a low melting point of about 50°·8 C. Hence it affords an interesting case of an acid in which the changes in position and character of the Raman lines could be followed up as it passes from solid to liquid and to solutions of varying concentration and the manner of electrolytic dissociation could be uniquely determined.

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[1] Venkateswaran, C. S., *Proc. Ind. Acad. Sci.*, A, 1935, **2**, 119; 1936, **3**, 25.

[2] Ganesan, A. S., *Proc. Ind. Acad. Sci.*, A, 1934, **1**, 156.

* The numbers in this and the subsequent pages denote the wavenumbers in cm^{-1}.

2. *Experimental.*

The experimental set up for this investigation was the same as those described by the author in the previous communications.[3,4] Hundred grams of pure crystalline selenic acid were supplied by Kahlbaum in a sealed tube and were used as such without further purification. Since the substance is highly hygroscopic, the sealed tube was kept intact during the investigation in the solid, molten and super-cooled states. The time of exposure for obtaining a satisfactory spectrogram was half an hour for the solid and twenty-four hours for the molten and the super-cooled liquid. In order to obtain a fairly quantitative estimate of the relative intensities of the lines in the aqueous solutions of varying concentration the product of the concentration and the time of exposure was kept constant, while the other conditions of experiment remained the same. The time of exposure for the 92·5% solution was twelve hours and was correspondingly increased for other concentrations. Specially backed Ilford " Golden Isozenith " plates were used for photographing the spectra. The plates were measured by means of a Hilger cross-slide microscope in comparison with an ion arc spectrum which was recorded in the centre of every picture.

3. *Results.*

Enlarged photographs of the spectra are reproduced in the accompanying plates and illustrate the changes in the Raman lines during the transition from solid to liquid and to the aqueous solutions. The concentrations are given as percentages of the solid per hundred grams of the solution. The schematic representation of lines in Fig. 1 shows clearly the changes in position and relative intensities of the lines as the dilution progresses. The thick dark lines are drawn with reference to a frequency scale in cm.$^{-1}$ units and their positions in the scale represent the frequency shifts corresponding to the maximum intensity of the banded Raman lines. The height of each dark line is proportional to the intensity of the corresponding modified line. The lines due to the same mode of vibration of the molecule in the different stages of dilution are joined together by dotted lines and their assignment is indicated below.

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[3] Venkateswaran, C. S., *Proc. Ind. Acad. Sci.*, A, 1935, **1**, 850; *loc. cit.*

[4] Venkateswaran, C. S., *Proc. Ind. Acad. Sci.*, A, 1936, **3**, 25.

TABLE I. (*Selenic acid.*)
Raman frequencies in cm.$^{-1}$.

State of Substance	1	2	3	4	5	6	7	8	9	10	11	12
Crystal ..	1383 (1)	..	930 ($\frac{1}{2}$) sh.	..	..	896 (5) sh.	..	778 (1)	766 (5) sh.	374 (2) sh.	355 (1) sh.	327 (1) sh.
Molten ..	..	1186 } (0) 1105 }	996 (3) 36	..	..	914 (8) 70	..	..	756 (10) 70	388 (6) 40	361 (6) 40	294 (3) 40
Super-cooled ..	..	..	978 (2) 32	..	..	899 (8) 30	..	..	752 (10) 30	387 (3) 16	360 (3) 16	294 (3) 20
92.5 ..	..	1160 (0) band	975 (1) 12	927 (2) 16	..	862 (5) 20	..	..	747 (10) 30	..	374 (5) 60	299 (5) 30
75 ..	..	..	..	934 (3) 20	..	826 (8) 16	..	..	748 (6) 20	..	390 (3) 50	307 (4) 30
50 ..	..	..	..	929 (3)	..	862 (10) 16	845 (0) sh.	..	742 (3) 20	..	390 (3) 40	312 (3) 30
30 ..	..	..	..	929 (2)	910 (0)	866 (10)	846 (1)	..	737 (3) 20	..	390 (3) 30	327 (3) 30
20 ..	..	..	..	925 (2)	908 (2)	866 (8)	845 (2)	..	732 (2) 20	..	398 (3) 20	332 (3) 20
15 ..	..	..	..	921 (1)	908 (2)	866 (8)	845 (4)	..	732 (1) 20	..	400 (3) 16	332 (3) 20
7.5 ..	..	..	..	921 (0)	908 (1)	866 (6)	845 (3)	..	732 (0) 20	..	402 (1) 16	332 (1) 20

Note.—The numbers within the brackets indicate visual estimate of intensities and the numbers below each frequency give the breadth of the line in cm.$^{-1}$.

Table I gives the frequency shifts of the centre of the Raman lines of the acid as solid, liquid and aqueous solutions of concentrations ranging from 92·5% to 7·5% by weight. Visual estimates of the intensities of the lines are given within brackets accompanying the corresponding line. The extension of the line to either side of its centre is given in wavenumber units below the frequency values.

4. *Discussion of Results.*

The Raman spectrum of the crystalline selenic acid consists of seven sharp lines of frequencies 930 ($\frac{1}{2}$), 896 (5), 778 (1), 766 (5), 374 (2), 355 (1)

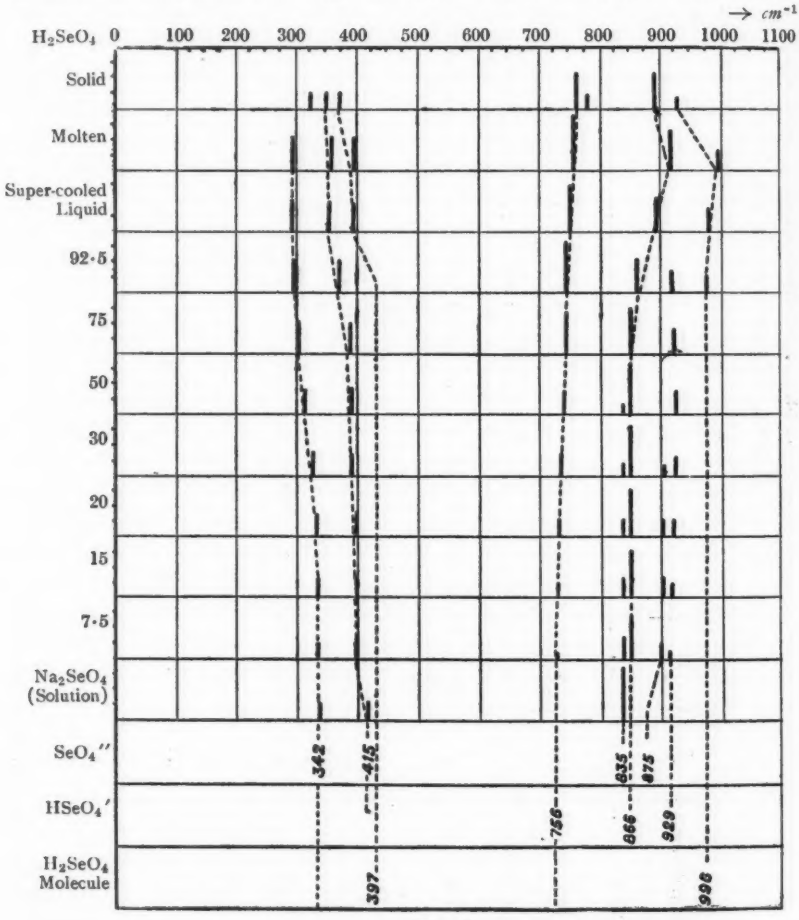

FIG. 1.

and 327 (1). Though the slit width employed throughout the experiment was a minimum (about 1/50 mm.), all the lines in the solid broaden out in the liquid and the solutions of high concentrations and tend to become sharper as the dilution increases. The lines undergo relative positional changes as can be inferred from the dotted lines indicating the course of each line in Fig. 1.

On melting the solid, the weak line 930 becomes a band of about 36 wavenumbers in width and undergoes a maximum shift of 66 wavenumbers towards higher frequency. In the super-cooled liquid this line as well as the other lines tend to approach that of the solid. The addition of a small quantity of water to the acid diminishes its intensity considerably and the frequency shift is also less than in the liquid state. At 75% this line practically disappears. But, instead, a new band makes its appearance first at 92·5% with a frequency shift of about 927 and increases in intensity from 92·5% to 30%. The centre of the line undergoes a gradual shift towards shorter frequency as dilution increases. At about 30% concentration this band at 927 shows a distinct doublet structure and for the lower concentrations it shows a clear asymmetry in intensity, the shorter frequency side increasing and the longer frequency side decreasing gradually in intensity. This is interpreted as due to the appearance of a new line at 910 at about 30% concentration, which is probably also present weakly at higher concentrations and which accounts for the apparent frequency shift of the line. The new line at 910 possesses a fairly constant frequency.

The line 896 which is one of the two intense lines in the solid phase has a finite breadth, but becomes very much broader (about 70 wavenumbers) and shifts towards a higher frequency of 914 in the liquid. The structure of this band is, however, different from that of the rest in the spectrum. It consists of a fairly broad line of maximum intensity at the centre and followed on either side by rotation wings. On the addition of water this line undergoes a marked change both in structure and position. In the 92·5% solution, it has only a breadth of about 20 wavenumbers. The frequency corresponding to maximum intensity is 862, thus undergoing a change of about 50 wavenumbers towards shorter frequency from the liquid to the solution. It has a constant frequency at all dilutions and becomes sharper at lower concentrations. The changes of intensity of this line are very striking. At 92·5% it is only half as intense as the one at 747 ; but at 75% its intensity is already slightly greater than that of the latter and goes on increasing up to about 30%. Though it continues to be the most intense line at lower concentrations, it appears to lose in intensity on further dilution. At

about 30% a new sharp line begins to make its appearance at 845 and gains in intensity as the dilution progresses.

The intense line at 766 and its faint companion at 778 of the solid appear as a single broad line (about 70 wavenumbers) in the molten state as well as at all dilutions. But this band changes in position progressively towards smaller frequency both during the transition from the solid to the liquid and on the addition of more and more of water. It appears as the most intense line in the liquid and in the solution of 92·5% concentration; but rapidly loses its intensity with dilution. At about 7·5% it is very faint and difficult to measure though it remains fairly broad. The extraordinary breadth of this line even at the highest dilution can be interpreted as due to the superposition of two diffuse lines, which in the solid show themselves as sharp lines. The change in the relative intensities of the two components also probably account to some extent for the frequency changes of the band towards the stronger line.

The two low frequencies at 274 and 355 in the solid state preserve the doublet character in the molten liquid, but in the solution appear as a single broad band (about 60 wavenumbers) which is asymmetrical in structure, being more intense towards shorter wavelength. The changes in the asymmetry of its structure in the solutions, however, show that the higher frequency component diminishes rapidly in intensity. The third low frequency at 327 in the solid, on the other hand, undergoes a degradation in frequency from the solid to liquid and becomes broad. It has almost the same frequency value at 92·5% solution as in liquid, but gradually increases towards higher frequency as the dilution progresses in the same manner as the band at 390. Though up to about 50% concentration the 390 band is broader than the one at 312, they are almost equal at 30% and at lower concentrations, there is a complete reversal in the relation between the widths of these two bands.

TABLE II. (*Sulphuric acid.*)
Raman frequencies in cm^{-1}.

Concentration	1	2	3	4	5	6	7	8	9
100% ..	..	562	911 (6) 30	..	..	..	1142	..	..
90% ..	408 (3) 60	565 (4) 60	911 (5) 35	970 (0)	..	1038 (4) 40	..	..	..
75% ..	418 (3) 60	579 (4) 60	905 (4) 40	..	..	1034 (5) 40	..	..	..
50% ..	426 (3) 60	588 (4) 60	897 (3) 50	..	982 (2) 20	1038 (5) 40	1172	1234	1341
30% ..	427 (3) 60	593 (4) 60	896 (2) 55	..	982 (6) 20	1047 (6) 30	1172	1223	1334
20% ..	429 (3) 60	592 (4) 60	895 (0) 60	..	983 (6) 20	1050 (6) 25	1168	1236	faint
10% ..	faint	592 (4) 60	895 (0) 60	..	983 (6) 20	1051 (6) 20	..	..	..

Besides these lines there is one line at 1383 in the solid and two diffuse lines at 1186 and 1105 in the liquid which appear as a broad band at 92·5% concentration.

The characteristic Raman band of water begins to show at 75% and gains rapidly in intensity as the dilution progresses. The triple structure of the band is difficult to identify but the relative intensities of the different portions of the unsymmetrical band agree fairly closely with that of pure water itself.

5. Comparison with Sulphuric Acid.

It is known that selenic acid is a strong acid comparable in strength with its analogue, sulphuric acid and it is to be expected that it should show an anomalous behaviour in its Raman spectra similar to that of the latter. The above picture of the changes in position, intensity and structure of the Raman lines, corresponds closely with similar observations by previous investigators[5] in sulphuric acid. For purposes of comparison the Raman frequencies of sulphuric acid solutions are reproduced in Table II from an exhaustive study of this acid by Bell and Jeppesen.[6] In general, the Raman spectra of the different solutions of this acid consists of four sets of lines namely,

(1) 911–895 and 1142 which are present in the 100% acid and drop off in intensity as it is diluted ; these are assigned to the undissociated molecules.

(2) 1038–1051 which is not present in the pure acid but which appears and rapidly becomes stronger on dilution ; this is attributed to HSO_4' ions.

(3) 982 which though present in 50% and perhaps also in 75% becomes appreciable only at concentrations lower than 25% ; this is characteristic of the SO_4'' ions.

(4) Those at 408–429 and 562–592 which are present at all concentrations and seem to belong to the ions and molecules alike.

Our results with selenic acid can also be classified as above.

(1) The lines 756–732, 996–976, 388–397 and 1186–1160 are present in the liquid and in 92·5% solution, but either totally disappear or drop off in intensity as the dilution increases. It is interesting to observe that the most intense line in this group, namely, 756–732 undergoes a shift towards a lower frequency just as the corresponding line 911–895 in the sulphuric acid.

(2) The lines 862 and 927–921 rapidly increase in intensity up to about 30% and remain intense throughout.

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[5] For complete references, see Angus and Leckie, *P.R.S.*, 1934, **149A**, 327.

[6] Bell, R. M., and Jeppesen, M. A., *J. Chem. Phys.*, 1935, **3**, 245.

(3) The lines 908 and 845 begin to appear faintly at about 50% and increase in intensity on further dilution. Unlike the corresponding line 982 of sulphuric acid, the line 845 never becomes a prominent line in the spectrum.

(4) The broad lines 360–402 and 294–332 are present at all concentrations as well as in the solid. They behave exactly like the lines 562–592 and 408–429 in sulphuric acid as regards positional changes.

There is, thus a close correspondence between the two spectra, the corresponding frequencies themselves being smaller in selenic acid as is to be expected because of the greater atomic weight of selenium.

Recently there has been a controversy regarding the frequency shifts of some of the lines in sulphuric acid. Woodward and Horner[7] have pointed out that the apparent shifts could be interpreted on the basis that the broad lines consist of components of slightly different frequencies which appear and disappear at different concentrations. Bell and Jeppesen,[8] however, disagree with the above authors and insist that the lines are symmetrical, and the shift is gradual and depends on the influence of the state of solution on the vibrations of the molecular species concerned.

As has been pointed out before, our results with selenic acid support the view put forward by Woodward and Horner regarding the composite nature of the broad lines. The bands in the selenic acid which undergo frequency variations show a doublet nature at a particular concentration and a marked asymmetry in their structure at other dilutions. In the solid, the corresponding lines are generally split up. The only exception to this is the low frequency at about 300. These observations were possible in the spectra of this acid because of the clearness of the picture in all states. But in the case of sulphuric acid, a strong continuous spectrum obscures finer details. In view of the close accordance between the results of selenic acid and sulphuric acid in other respects, it seems probable that in the case of the latter also the diffuse Raman lines consist of relatively narrow components as suggested by Woodward and Horner. It should, however, be pointed out that the complete drift of the lines due to changing concentrations could not be accounted for mainly on the basis of components.

6. *Electrolytic Dissociation of Selenic Acid.*

From what has been stated in the previous section, it will be clear that the anomalous variation in intensity and frequency shifts that are observed in the Raman lines in selenic acid could be explained in the same manner as in the case of sulphuric acid, namely, by assuming that this acid, like the

[7] Woodward and Horner, *Proc. Roy. Soc.*, A, 1934, **144**, 129.

[8] Bell, R. M., and Jeppesen, M. A., *loc. cit.*

latter ionises in two stages, first from $H_2SeO_4 \rightarrow HSeO_4' + H^\circ$ and then from $HSeO_4' \rightarrow SeO_4'' + H^\circ$. On the basis of this hypothesis the band 756–732 which is prominent in the molten condition and falls off in intensity gradually in aqueous solutions, is characteristic of the undissociated molecules. The lines with frequency shifts of 1186, 1105, 996–976 and 388 which are present only at 100% liquid and 92·5% solution also arise from the H_2SeO_4 molecules. The second intense line at 862 which gains rapidly in intensity as the concentration falls from 92·5% to 30% and the line at 927 are to be attributed to the first ionisation product, $HSeO_4'$ ions. The frequency shifts observed for $KHSeO_4$[9] are 852 and 339. The close agreement between the line 852 in the biselenate and 862 assigned to $HSeO_4'$ ion lends support to the above conclusion. Its presence in the 100% acid shows that, as is not the case with sulphuric acid, a certain proportion of molecules in the solid and the liquid states has undergone partial dissociation from H_2SeO_4 to $HSeO_4'$. The great intensity of this line in most of the concentrations is due to the preponderance over all others of the $HSeO_4$ ions which give rise to it and shows its remarkable stability in the aqueous solutions. The line at 845 which makes its appearance first at 50% and gains steadily in intensity on further dilution, as well as the line at 908 are to be attributed to the normal vibrations of the SeO_4'' ions. This indicates that the second stage of ionisation from $HSeO_4' \rightarrow SeO_4'' + H^\circ$ begins only at 50% and even at 7·5% it is not appreciable. The two low frequencies 361–402 and 294–332 appear to be common to all the three molecular species.

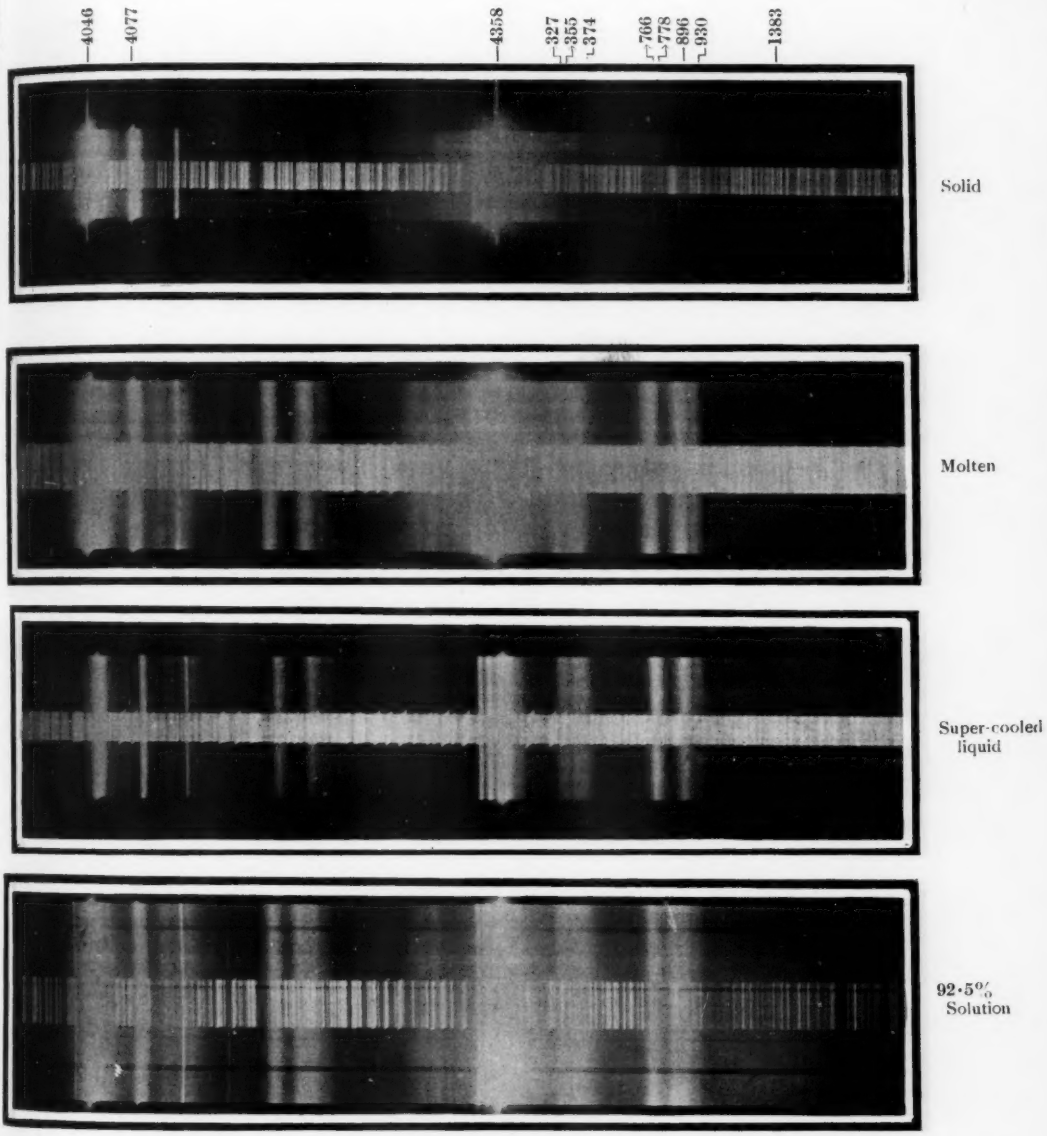
In Table III the frequencies assigned to SeO_4'' and SO_4'' ions in the acids are compared with the corresponding frequencies in selenates[10] and sulphates[11] respectively.

TABLE III.

SeO_4'' (in 7·5% acid) ..	332	402	845	908
SeO_4'' (in Selenate) ..	342	415	835	875
SO_4'' (in 10% acid) ..	418	597	982	1168
SO_4'' (in Sulphate)° ..	447	623	983	1115

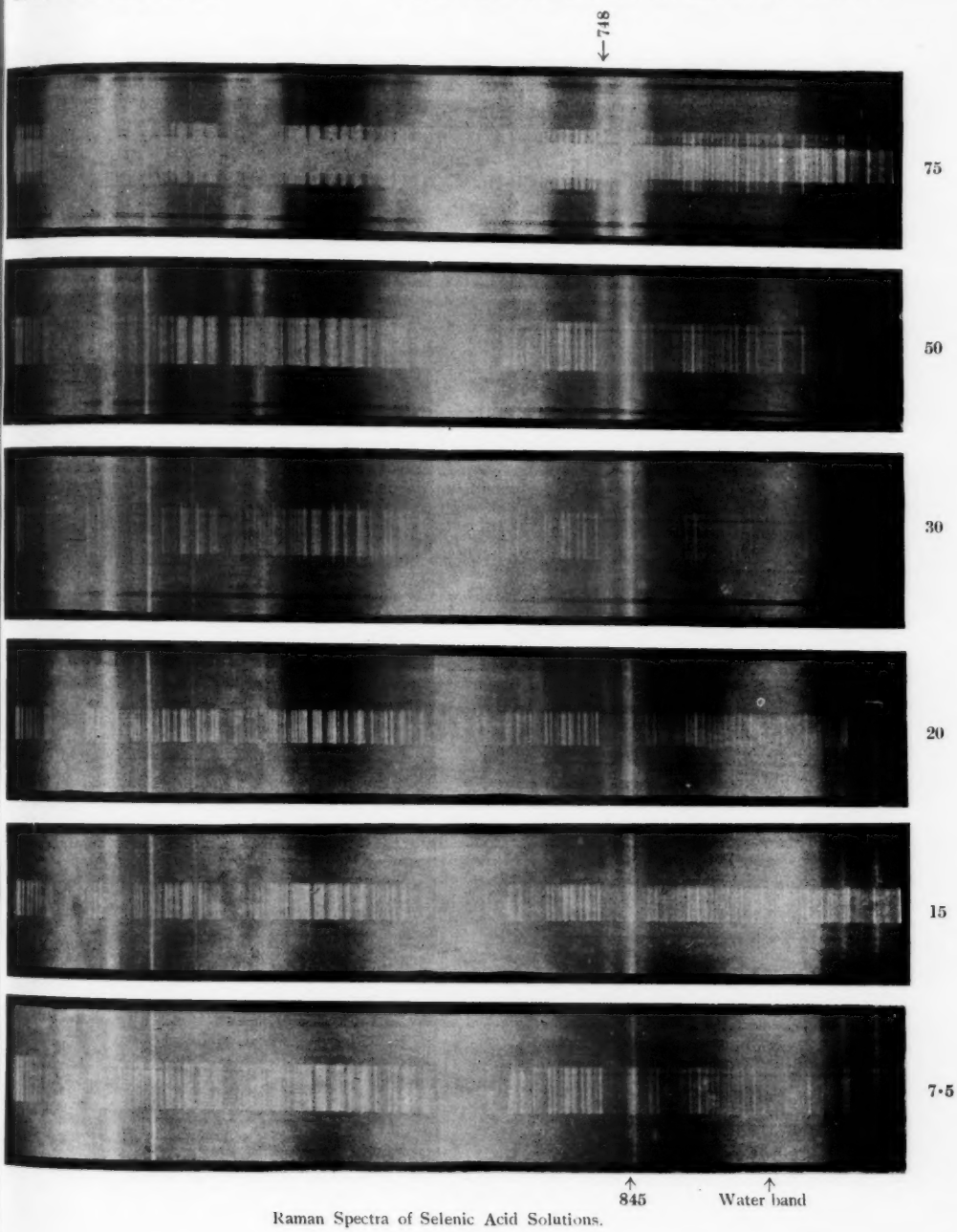
It is interesting to note a systematic variation in frequencies in both SeO_4'' and SO_4'' ions while passing from the acid to the salt. The close agreement between the values of the Raman lines arising from SeO_4'' in the acid and the selenates, lends support to the above interpretation of the results. The

[9] Pringsheim and Yost, *Zeit. f. Physik*, 1929, **58**, 1.
[10] A. S. Ganesan, *loc. cit.*
[11] Kohlrausch, *Der Smekal-Raman Effect*, 1931.



Raman Spectra of Selenic Acid

(Solid, Liquid and Solution).



Raman Spectra of Selenic Acid Solutions.

presence of the line at 732 even at 7·5% solution shows that a certain proportion of the H_2SeO_4 molecules exists even at those dilutions. It is very difficult to say whether the SeO_4'' ions are produced by the direct dissociation of H_2SeO_4 to $2H^\circ$ and SeO_4'' or only from the first ionisation product $HSeO_4'$ which appears to be very stable. In general, the results indicate that selenic acid possesses a lower degree of ionisation than sulphuric acid.

The absence of any line in the spectrum of selenic acid at about 2312 corresponding to the Raman line in liquid hydrogen selenide[12] signifies that no H–Se bond is present in the molecule.

7. Change of State and Raman Effect.

The influence of change of state from the solid to liquid on the Raman lines of this acid is illustrated in the accompanying plate. Two distinct changes occur on the lines, namely, a shift towards longer wavelength of all the lines except 766 and 327 which have a reverse effect and a general broadening. In the super-cooled liquid these effects are, to some extent, less pronounced. In general, these changes of the lines following the change of state are characteristic of hetro-polar compounds.[13] Their full significance will be discussed in a separate paper along with the results of selenious acid.*

In conclusion the author wishes to express his thanks to Sir C. V. Raman for his kind interest in the work.

Summary.

The Raman spectrum of selenic acid has been investigated in the state of solid, liquid and aqueous solutions of concentrations varying from 92·5% to 7·5% by weight. The solid has yielded eight lines with frequency values of 1383, 930, 896, 778, 766, 374, 355 and 327. Marked changes in position, intensity and character of these lines are observed during the transition from the solid to the liquid and then to the aqueous solutions. The gradual disappearance of some of the lines and the increase in the intensity of some others and the appearance of new lines are explained on the basis of the stepwise dissociation of the acid, namely, $H_2SeO_4 \rightarrow HSeO_4' + H^\circ$ and $HSeO_4' \rightarrow SeO_4'' + H^\circ$. The results indicate that the first stage of ionisation starts from the solid and the second stage from about 50% concentration. The results are compared with those of its analogue, sulphuric acid and conclusions are drawn regarding the structure and the apparent shifts of the bands in both these acids. The changes that take place in the lines during the transition from the solid to the liquid are characteristic of the hetro-polar nature of the chemical bond in the acid molecules.

[12] Dadieu and Engler, *Wien Anz.*, 1935.

[13] Venkateswaran, C. S., *Proc. Ind. Acad. Sci.*, A, 1935, **2**, 260.

* Unpublished work of the author.

THE NEUTRINO THEORY OF LIGHT.

By Max Born
and
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Received March 18, 1936.

1. Introduction.

The most important contribution during the last years to the fundamental conceptions of theoretical physics seems to be the development of a new theory of light which contains the acknowledged one as a limiting case, but connects the optical phenomena with those of a very different kind, radioactivity. The idea that the photon is not an elementary particle but a secondary one, composed of simpler particles, has been first mentioned by P. Jordan[1]. His argument was a statistical one, based on the fact, that photons satisfy the Bose-Einstein statistics. It is known from the theory of composed particles as nuclei, atoms or molecules, that this statistics may appear for such systems, which are compounds of elementary particles satisfying the Fermi-Dirac statistics (*e.g.*, electrons or protons). After the discovery of the neutrino, de Broglie[2] suggested that a photon $h\nu$ is composed of a " neutrino " and an " anti-neutrino," each having the energy $\frac{1}{2}h\nu$. He has developed some interesting mathematical relations between the wave equation of a neutrino (which he assumed to be Dirac's equation for a vanishingly small rest-mass) and Maxwell's field equations. But de Broglie has not touched the central problem, namely, as to how the Bose-Einstein statistics of the photons arises from the Fermi-statistics of the neutrinos. This question cannot be solved in the same way as in the cases mentioned above (material particles) where it is a consequence of considering the composed system as a whole neglecting internal motions. This is possible because of the strong forces keeping the primary particles together. But in the case of neutrinos we have no knowledge of such forces, and it would contradict the simplicity of de Broglie's idea to introduce them.

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[1] P. Jordan, "Die Lichtquanten hypothese," *Erg. der Exakt. Naturw.*, 1928, **17**, 158. P. Jordan, *Zeits. f. Phys.*, 1935, **93**, 464; 1936, **98**, 709 and 759; 1936, **99**, 109.

[2] L. de Broglie, *C.R.*, 1932, **195**, 536, 577, 862; 1933, **197**, 1377; 1934, **198**, 135; 1934, **199**, 445, 1165. A coherent representation is to be found in his book *Une Nouvelle Conception de la Lumiere* (181, Act. Sci. et Ind.). Further L. de Broglie and J. Winter, *C.R.*, 1934, **199**, 813.

This fundamental problem has been solved by Jordan. He has shown that no forces between neutrinos are required but the way of their interaction with electric charges leads to the effect that pairs of neutrinos behave generally as photons. Jordan has formulated the principles involved and has proved rather deep mathematical theorems expressing the relation of neutrinos and photons. The fuller development of the mathematical method is due to R. de L. Kronig[3] who is working in close co-operation with Jordan. We shall give here a report on the present situation, as far as it has come to our knowledge and hope that this will be welcome to the readers, not only because the original papers are scattered over several periodicals but are extremely difficult to read as they contain some apparent contradictions which have not been avoided even in the latest paper.

We disagree with Jordan and Kronig only in one essential point. It is that we see no reason to introduce the spin of the neutrino, but that we can describe the difference between the two kinds of neutrinos in the same way as the difference between electrons and positrons in Dirac's theory of holes.

We have tried to make this report comprehensive without much recourse to literature.

2. *The Neutrino.*

The particles which physics considers to-day as elementary can be ordered corresponding to their masses in 3 groups, each containing two types :

1. Particles of great mass : proton, neutron ;
2. Particles of small mass : electron, positron ;
3. Particles of zero mass : photon, neutrino.

The central problem of future physics is the explanation of the existence of these different types of particles and the derivation of their properties from a fundamental principle. As to the first two groups, we think that the solution must lie in the direction of a non-linear field theory, as has been tried to develop.[4] But the particles of the third group correspond classically to the case of very weak field, where the non-linearity plays no rôle. This limiting case was generally assumed to be known with any desired accuracy, as represented by the quantised field equations of Maxwell. But the discovery of the neutron has shaken this conviction and we are compelled to revise the very principles even of the limiting case, before we can hope to tackle the (probably non-linear) laws governing the higher particles.

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[3] R. de L. Kronig, *Physica*, 1935, **2**, 491, 854, 968.
[4] M. Born, *Proc. Roy. Soc.*, (A), 1934, **143**, 410.

The experimental facts which lead Pauli to the assumption of neutrinos are connected with the β-decay of radio-active nucleii. The spectrum of the emitted electrons (or positrons in the case of induced radio-activity) is continuous and has a wide range of velocity. But the emitting nucleus and the resulting nucleus are in every respect definite systems. All attempts to account for this fact by a simultaneous emission of γ-rays have failed.

There are only two ways of explanation : either the law of the conservation of energy does not hold in these cases or there are particles emitted which cannot be detected by our experimental methods, because of their extreme penetrating power.

To avoid the first unpleasant alternative,* Pauli has put forward the idea that very light, uncharged particles are emitted simultaneously with the electron when a neutron is converted into a proton (or *vice versa*), and he has called them *neutrinos*. It is not quite hopeless to prove their existence by using very light atoms made radio-active with the help of Fermi's method of neutron bombardment. One could observe the recoil of these atoms when emitting the electrons and measure the energy and momentum of both the particles. If there is a third particle involved in the process, its energy E and momentum p should be connected by the relativistic relation $\frac{E^2}{c^2} - p^2 = m_0^2 c^2$ where c is the velocity of light and m_0 its rest-mass. If m_0 turns out to be constant (for instance zero), there could be no doubt about the existence of the neutrino. Experiments of this kind have been undertaken in the Cavendish laboratory at Cambridge.[5]

Fermi[6] has shown that the hypothesis of neutrino emission for β-decay together with some simple and natural assumption about the interaction energy leads to a definite law of distribution for the emitted β-rays which is in good agreement with observation, if the rest-mass of the neutrino is taken as very small, very much smaller than that of the electron. It seems very probable that the rest-mass is exactly zero just as that of the photon.

These meagre facts are the experimental evidence on which the neutrino theory of light is based. *The leading idea is that the neutrinos are the primary*

---

* New experimental results of R. S. Shankland (*Phy. Rev.*, 1936, **49**, 8) on the Compton Effect (simultaneous emission of photons and electrons) indicate a failure of the conservation laws. P. A. M. Dirac has, therefore, concluded (*Nature*, 1936, **137**, 298) that the said laws have to be given up. Nevertheless, we think it worth while to study carefully the possible way out of this dilemma pointed out by the neutrino theory.

[5] Bainbridge [*Science*, 1936, **83**, 38 (Suppl.)] claims to have a direct proof of the existence of the neutrino from considerations about the stability of isotopes.

[6] E. Fermi, *Nuovo Cimento*, 1934, **11**, 1.

particles moving with the velocity of light, and that the processes usually described in terms of photons or light waves are really simultaneous actions of several neutrinos.

Jordan and de Kronig have followed de Broglie in the assumption that there are two kinds of neutrinos, neutrinos and anti-neutrinos, differing by their spin. This is the only point where we do not agree with them. *We have found that the whole theory could be developed by assuming only one kind of neutrino which can have positive or negative energy.* Since in the thermal equilibrium at absolute zero all negative states are occupied, the total negative energy becomes infinite. This inconvenience is overcome by using the number of unoccupied states as variables and to call them anti-neutrinos, just as in Dirac's theory of holes representing positrons. But whereas in the case of the electrons, the formulation of this theory of holes leads to great difficulties,[7] arising from the external fields which have to be taken into account, it is very simple and satisfactory here in the case of the neutrinos which are not attacked by external forces.

3. *Fermi Statistics of Neutrinos.*

We describe the motion of the neutrinos and anti-neutrinos with the help of two infinite sets of non-commuting variables a_κ, γ_κ which we numerate (for sake of convenience) with the help of half numbers, $\kappa = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \cdots\cdots$ We define the a_κ, γ_κ also for negative indices with the help of the relations:*

$$(1)\quad a_{-\kappa} = \gamma_\kappa{}^\dagger\,; \qquad \gamma_{-\kappa} = a_\kappa{}^\dagger, \qquad \kappa > 0$$

where the † means the adjoint operator.

The meaning of these variables can be described, using the correspondence principle, as Fourier-coefficients of wave functions; for instance in one dimension

$$(2)\quad \begin{cases} \psi\,(t - x/c) = \sum\limits_{\kappa=-\infty}^{\infty} a_\kappa\, e^{2\pi i \nu_1 \kappa (t - x/c)}, \\ \chi\,(t - x/c) = \sum\limits_{\kappa=-\infty}^{\infty} \gamma_\kappa\, e^{2\pi i \nu_1 \kappa (t - x/c)} = \psi^\dagger, \end{cases}$$

where ν_1 corresponds to the fundamental frequency of the waves in the finite space considered (Hohlraum). We can interpret κ as the positive or negative energy of the corresponding state in units of $h\nu_1$.

---

[7] W. Heisenberg, *Zeits. f. Phy.*, 1934, **90**, 209; and 1936, **98**, 714.
P. A. M. Dirac, *Proc. Camb. Phil. Soc.*, 1934, **45**, 245; and *Quantum Mechanics*, 1935, Chap. 13.

* There is really no use of using two kinds of variables; we introduce the γ_κ only to be in conformity with Jordan and to have symmetry between neutrinos and anti-neutrinos.

The functions ψ, χ are not self-adjoint; but $\chi = \psi^\dagger$. Instead of using the states of negative energy, one can introduce the holes amidst the states; the wave function describing them is $\chi = \psi^\dagger$ and to each positive energy κ belongs a neutrino (ψ, or a_κ) and a hole or anti-neutrino (χ or γ_κ).

We postulate the following commutation laws:

$$(3)\quad \begin{cases} a_\kappa a_\mu + a_\mu a_\kappa = 0 \\ \gamma_\kappa \gamma_\mu + \gamma_\mu \gamma_\kappa = 0 \\ \gamma_\kappa a_\mu + a_\mu \gamma_\kappa = \delta_{\mu,-\kappa}. \end{cases}$$

The number of neutrinos and anti-neutrinos of energy κ is defined only for $\kappa > 0$ by the operators

$$(4)\quad \begin{cases} N_\kappa^{(+)} = a_\kappa^\dagger a_\kappa = 1 - a_\kappa a_\kappa^\dagger \\ N_\kappa^{(-)} = \gamma_\kappa^\dagger \gamma_\kappa = 1 - \gamma_\kappa \gamma_\kappa^\dagger. \end{cases}$$

There are two other expressions for each of these quantities with the help of (1).

It is well known that these operators (4) have only the eigenvalues 0, 1, which mean unoccupied or occupied state. As we do not suppose extended knowledge of literature, we shall explain this a little closer in the next section.

4. Matrix Representation of the Fundamental Operators.

We start with a simple case and define the matrices*

$$(5)\quad a = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix};\quad a^\dagger = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix};\ \text{and}\ s = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix};$$

which satisfy the following relations:

$$(6)\quad \begin{cases} a^2 = 0 & a^{\dagger 2} = 0 & s^2 = 1 \\ a^\dagger a + a a^\dagger = 1 & as + sa = 0 & a^\dagger s + s a^\dagger = 0. \end{cases}$$

The matrix a is useful to describe a system with one state which could be occupied by a particle or not. We define the "number of particles" in this state which is of course either 0 or 1, with the help of the matrix

$$(7)\quad a^\dagger a = n = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix},$$

which is diagonal and has the eigenvalues 0 and 1.

Thus from (5) it follows that

$$(8)\quad a a^\dagger = 1 - n.$$

We remark that one has

$$(9)\quad s = 1 - 2n$$

but we do not enter in a more elaborate discussion of the interesting formalism connected with these matrices. Now we extend this method to systems with

---

* They are closely connected with Pauli's spin matrices:

$$\sigma_x = a^\dagger + a;\ \sigma_y = i(a^\dagger - a);\ \text{and}\ \sigma_z = s.$$

more than one state, occupied or not, by introducing the notion of the direct product of matrices.

5. Direct Product of Matrices.

If $a = (a_{kl})$ and $b = (b_{mn})$ are two matrices, the direct product is given by

(10) $\quad a \times b = (a_{kl} \cdot b_{mn})$

i.e., the elements are all products of any element of a with any element of b.

(11) $\quad (a \times b)_{km,\, ln} = a_{kl} b_{mn}.$

If $a \times b = 0$ it follows that either $a = 0$ or $b = 0$.

Further

(12) $\quad (a \times b)^\dagger = \{(a \times b)^\dagger{}_{ln,\, km}\} = (a_{lk}{}^\dagger\, b_{nm}{}^\dagger) = a^\dagger \times b^\dagger.$

6. Representation of a_κ and γ_κ.

We now give a representation of the matrices a_κ and γ_κ fulfilling (3) with the help of the direct products of matrices consisting of the fundamental matrices a and s. This representation was discovered by Jordan and Wigner[8] who have also shown that the solution is unique apart from unitary transformations. Their representation is given by the scheme (next page).

Using the definition (10) of the direct product of matrices and the equations (6), (11) and (12), it can be easily verified that the representations of the fundamental operators given in (13) satisfy the commutation rules (3).

7. A New Set of Operators a_κ and c_κ.

We will now define, as Jordan has done, a new set of operators as functions of our fundamental operators a_κ and γ_κ.

They are

$$(15) \qquad a_\kappa = \frac{a_\kappa + \gamma_\kappa}{\sqrt{2}}, \qquad c_\kappa = \frac{a_\kappa - \gamma_\kappa}{i\sqrt{2}}.$$

From (15) we can express a_κ and γ_κ as functions of a_κ and c_κ:

$$(16) \qquad a_\kappa = \frac{a_\kappa + ic_\kappa}{\sqrt{2}}, \qquad \gamma_\kappa = \frac{a_\kappa - ic_\kappa}{\sqrt{2}}.$$

From (15) and (1) we see that

$$(17) \quad \kappa > 0 \qquad a_{-\kappa} = \frac{a_{-\kappa} + \gamma_{-\kappa}}{\sqrt{2}} = \frac{\gamma_\kappa{}^\dagger + a_\kappa{}^\dagger}{\sqrt{2}} = a_\kappa{}^\dagger, \qquad c_{-\kappa} = \frac{a_{-\kappa} - \gamma_{-\kappa}}{i\sqrt{2}} = \frac{\gamma_\kappa{}^\dagger - a_\kappa{}^\dagger}{i\sqrt{2}} = c_\kappa{}^\dagger.$$

[8] P. Jordan and E. Wigner, *Zeits. f. Phy.*, 1928, **47**, 631.

(13) $\kappa > 0$

	$\frac{1}{2}$, $-\frac{1}{2}$, $\frac{1}{2}$, $-\frac{1}{2}$, $--$, $(\kappa-1)$, $-(\kappa-1)$, κ, $-\kappa$, $(\kappa+1)$, $-(\kappa+1)$, $--$
$a_\kappa = \gamma_{-\kappa}^+$	$s \times s \times s \times s \times -- \times s \times s \times a \times 1 \times 1 \times 1 \times --$
$a_{-\kappa} = \gamma_\kappa^+$	$s \times s \times s \times s \times -- \times s \times s \times s \times a^+ \times 1 \times 1 \times --$
$\gamma_\kappa = a_{-\kappa}^+$	$s \times s \times s \times s \times -- \times s \times s \times s \times a \times 1 \times 1 \times --$
$\gamma_{-\kappa} = a_\kappa^+$	$s \times s \times s \times s \times -- \times s \times s \times s \times a^+ \times 1 \times 1 \times --$

Each matrix has only one non-vanishing element given by the following scheme in which t_κ is equal to zero or unity.

(14) $\kappa > 0$

$$\begin{cases} a_\kappa\ (t_{\frac{1}{2}}, t_{-\frac{1}{2}}, --, 0, t_{-\kappa}, -- ; t_{\frac{1}{2}}, t_{-\frac{1}{2}}, -- , 1, t_{-\kappa}, --) \equiv (-)^{t_{\frac{1}{2}}+t_{-\frac{1}{2}}+\cdots+t_{-(\kappa-1)}} \\ a_{-\kappa}\ (t_{\frac{1}{2}}, t_{-\frac{1}{2}}, --, t_\kappa, 1, -- ; t_{\frac{1}{2}}, t_{-\frac{1}{2}}, -- , t_\kappa, 0, --) \equiv (-)^{t_{\frac{1}{2}}+t_{-\frac{1}{2}}+\cdots+t_\kappa} \\ \gamma_\kappa\ (t_{\frac{1}{2}}, t_{-\frac{1}{2}}, --, t_\kappa, 0, -- ; t_{\frac{1}{2}}, t_{-\frac{1}{2}}, -- , t_\kappa, 1, --) \equiv (-)^{t_{\frac{1}{2}}+t_{-\frac{1}{2}}+\cdots+t_\kappa} \\ \gamma_{-\kappa}\ (t_{\frac{1}{2}}, t_{-\frac{1}{2}}, --, 1, t_{-\kappa}, -- ; t_{\frac{1}{2}}, t_{-\frac{1}{2}}, -- , 0, t_{-\kappa}, --) \equiv (-)^{t_{\frac{1}{2}}+t_{-\frac{1}{2}}+\cdots+t_{-(\kappa-1)}} \end{cases}$$

From (15) and (3), we obtain the commutation rules for the operators a_κ and c_κ.

$$
\begin{aligned}
a_\kappa\, a_\mu + a_\mu\, a_\kappa &= \delta_{\mu,-\kappa}\,; \\
c_\kappa\, c_\mu + c_\mu\, c_\kappa &= \delta_{\mu,-\kappa}\,; \\
a_\kappa\, c_\mu + c_\mu\, a_\kappa &= 0\,;
\end{aligned} \tag{18}
$$

for $\kappa, \mu = \pm \tfrac{1}{2}, \pm \tfrac{3}{2}, \pm \tfrac{5}{2}, \cdots$

As the new operators a_κ and c_κ obey the commutation rules (18), a Jordan-Wigner representation can be developed for them. Thus $a_{-\kappa}\, a_\kappa$ or $a_\kappa{}^+ a_\kappa$ has the eigenvalues 0 and unity. Similar is the case of $c_{-\kappa}\, c_\kappa$ or $c_\kappa{}^+\, c_\kappa$. We define operators connected with these as

$$
\begin{aligned}
\mathrm{L}_\kappa &= a_\kappa{}^+ a_\kappa = a_{-\kappa}\, a_\kappa\,; \\
\mathrm{N}_\kappa &= c_\kappa{}^+\, c_\kappa = c_{-\kappa}\, c_\kappa\,;
\end{aligned} \tag{19}
$$

for $\kappa > 0$.

From (15) and (19) we find easily,

$$
\begin{aligned}
\mathrm{L}_\kappa &= \tfrac{1}{2}\,(\mathrm{N}_\kappa{}^{(+)} + \mathrm{N}_\kappa{}^{(-)}) + \tfrac{1}{2}\,(a_\kappa{}^+\, \gamma_\kappa + \gamma_\kappa{}^+\, a_\kappa), \\
\mathrm{N}_\kappa &= \tfrac{1}{2}\,(\mathrm{N}_\kappa{}^{(+)} + \mathrm{N}_\kappa{}^{(-)}) - \tfrac{1}{2}\,(a_\kappa{}^+\, \gamma_\kappa + \gamma_\kappa{}^+\, a_\kappa),
\end{aligned} \tag{20}
$$

or

$$
\begin{aligned}
\mathrm{L}_\kappa + \mathrm{N}_\kappa &= \mathrm{N}_\kappa{}^{(+)} + \mathrm{N}_\kappa{}^{(-)}, \\
\mathrm{L}_\kappa - \mathrm{N}_\kappa &= a_\kappa{}^+\, \gamma_\kappa + \gamma_\kappa{}^+\, a_\kappa.
\end{aligned} \tag{21}
$$

From the representation (13) of the a_κ, γ_κ one sees that $\mathrm{L}_\kappa - \mathrm{N}_\kappa$ has no diagonal elements, or the expectation value

$$
\bar{\mathrm{L}}_\kappa - \bar{\mathrm{N}}_\kappa = 0. \tag{22}
$$

$\mathrm{N}_\kappa{}^{(+)}$ and $\mathrm{N}_\kappa{}^{(-)}$ are the numbers of neutrinos and anti-neutrinos in the state κ. We can assume that all states above a certain state are unoccupied,

$$
i.e., \qquad \mathrm{N}_\kappa{}^{(+)} = 0 \quad \text{and} \quad \mathrm{N}_\kappa{}^{(-)} = 0, \quad \text{for } \kappa > \mathrm{K}.
$$

Therefore

$$
\sum_\kappa (\mathrm{L}_\kappa + \mathrm{N}_\kappa) \text{ is finite.} \tag{23}
$$

From (22) it follows, that all eigenvalues of

$$
\sum_\kappa (\bar{\mathrm{L}}_\kappa - \bar{\mathrm{N}}_\kappa) = \overline{\sum_\kappa (\mathrm{L}_\kappa - \mathrm{N}_\kappa)} \tag{23}
$$

are finite. Therefore

$$
\sum_\kappa \mathrm{L}_\kappa \quad \text{and} \quad \sum_\kappa \mathrm{N}_\kappa \text{ are finite}\,; \qquad \kappa > 0. \tag{24}
$$

We shall make use of these results later.

With the help of the operators a_κ and c_κ we will presently define the important operator b_ξ first discovered by Jordan which obeys the Bose-Einstein commutation rules.

8. *The Operator* b_k.

Jordan has defined the operator b_k as

$$b_k = \frac{i}{\sqrt{|k|}} \sum_{\kappa=-\infty}^{\infty} a_\kappa \, c_{k-\kappa} \tag{25}$$

for $k = \pm 1, \pm 2, \pm 3, \cdots$

We first observe that

$$b_k^+ = b_{-k} \tag{26}$$

for

$$b_k^+ = -\frac{i}{\sqrt{|k|}} \sum c_{k-\kappa}^+ a_\kappa^+ = \frac{i}{\sqrt{|k|}} \sum_{-\infty}^{\infty} a_\kappa^+ c_{k-\kappa}^+$$

$$= \frac{i}{\sqrt{|k|}} \sum_{-\infty}^{\infty} a_{-\kappa} c_{-k+\kappa} = \frac{i}{\sqrt{|k|}} \sum_{-\infty}^{\infty} a_\kappa c_{-k-\kappa} = b_{-k}$$

We will now obtain the commutation rules for b_k.

$$[b_k, b_j] = (b_k b_j - b_j b_k) = -\frac{1}{\sqrt{|kj|}} \sum_{\kappa,\iota} [a_\kappa c_{k-\kappa}, a_\iota c_{j-\iota}],$$

$$[a_\kappa c_{k-\kappa}, a_\iota c_{j-\iota}] = a_\kappa [c_{k-\kappa}, a_\iota c_{j-\iota}] + [a_\kappa, a_\iota c_{j-\iota}] c_{k-\kappa}$$

$$= -a_\kappa a_\iota \{c_{k-\kappa}, c_{j-\iota}\} + \{a_\kappa, a_\iota\} c_{j-\iota} c_{k-\kappa}$$

$$= -a_\kappa a_\iota \delta_{k-\kappa, -j+\iota} + c_{j-\iota} c_{k-\kappa} \delta_{\kappa, -\iota}. \tag{27}$$

Thus

$$[b_k, b_j] = \frac{1}{\sqrt{|kj|}} \sum_{-\infty}^{\infty} (a_\kappa a_{k+j-\kappa} - c_{j+\kappa} c_{k-\kappa}). \tag{28}$$

To evaluate the series we remember the result (24) that

$$\sum_\kappa L_\kappa = \sum_\kappa a_{-\kappa} a_\kappa \quad \text{and} \quad \sum_\kappa N_\kappa = \sum_\kappa c_{-\kappa} c_\kappa \tag{29}$$

are convergent. We further assume that the series

$$\sum_{\frac{1}{2}}^{\infty} a_{-\kappa+r} a_\kappa \quad \text{and} \quad \sum_{\frac{1}{2}}^{\infty} c_{-\kappa+r} c_\kappa \tag{30}$$

for any finite r, are convergent.*

Now we reorder the expression (28) in such a way that only terms of the form (30) appear:

$$\sqrt{|kj|}\,[b_k, b_j] = -\sum_{\frac{1}{2}}^{\infty} a_{k+j-\kappa} a_\kappa + \sum_{\frac{1}{2}}^{\infty} c_{k-\kappa} c_{j+\kappa} +$$

---

* This condition which has not been explicitly stated by Jordan, but which he really uses, seems to us to be indispensable.

$$+ \sum_{-\frac{1}{2}}^{-\infty} a_\kappa\, a_{k+j-\kappa} - \sum_{-\frac{1}{2}}^{\infty} c_{j+\kappa}\, c_{k-\kappa}$$

$$= -\sum_{\frac{1}{2}}^{\infty} a_{k+j-\kappa}\, a_\kappa + \sum_{\frac{1}{2}}^{\infty} c_{k-\kappa}\, c_{j+\kappa} + \sum_{\frac{1}{2}}^{\infty} a_{-\kappa}\, a_{k+j+\kappa} - \sum_{\frac{1}{2}}^{\infty} c_{j-\kappa}\, c_{k+\kappa}.$$

Replacing in the third series $-\kappa$ by $k+j-\kappa$ and in the fourth series $-\kappa$ by $k-j-\kappa$, we get

$$\sqrt{|k\,j|}\,[b_k, b_j] = -\sum_{\frac{1}{2}}^{\infty} a_{k+j-\kappa}\, a_\kappa + \sum_{\frac{1}{2}}^{\infty} c_{k-\kappa}\, c_{j+\kappa}$$

$$+ \sum_{k+j+\frac{1}{2}}^{\infty} a_{k+j-\kappa}\, a_\kappa - \sum_{k-j+\frac{1}{2}}^{\infty} c_{k-\kappa}\, c_{j+\kappa} \tag{32}$$

or

$$= -\sum_{\frac{1}{2}}^{k+j-\frac{1}{2}} a_{k+j-\kappa}\, a_\kappa + \sum_{\frac{1}{2}}^{k-j-\frac{1}{2}} c_{k-\kappa}\, c_{j+\kappa} = \tag{33}$$

$$-\tfrac{1}{2}\sum_{\frac{1}{2}}^{k+j-\frac{1}{2}} (a_{k+j-\kappa}\, a_\kappa + a_\kappa\, a_{k+j-\kappa}) + \tfrac{1}{2}\sum_{\frac{1}{2}}^{k-j-\frac{1}{2}} (c_{k-\kappa}\, c_{j+\kappa} + c_{j+\kappa}\, c_{k-\kappa}).$$

Thus using the commutation rules (18)

$$\sqrt{|k\,j|}\,[b_k, b_j] = 0, \qquad \text{if } k+j \neq 0.$$

If $k+j=0$

$$k\,[b_k, b_{-k}] = \tfrac{1}{2}\sum_{\frac{1}{2}}^{2k-\frac{1}{2}} (c_{k-\kappa}\, c_{-k+\kappa} + c_{-k+\kappa}\, c_{k-\kappa}) = \tfrac{1}{2}\cdot 2k$$

$$= k. \tag{34}$$

Thus we get the commutation rules for b_k as

$$\begin{aligned} b_k\, b_j - b_j\, b_k &= 0, \qquad \text{if } k+j \neq 0, \\ b_k\, b_{-k} - b_{-k}\, b_k &= 1, \qquad\quad k > 0. \end{aligned} \tag{35}$$

9. Expression for b_k in Terms of a_κ and γ_κ.

If we substitute in the expression (25) for b_k, a_κ, γ_κ instead of a_κ, c_κ with the help of (15) we get

$$\sqrt{|k|}\, b_k = \tfrac{1}{2}\sum_{-\infty}^{\infty} (a_\kappa + \gamma_\kappa)(a_{k-\kappa} - \gamma_{k-\kappa})$$

$$= \tfrac{1}{2}\sum_{-\infty}^{\infty} (a_\kappa\, a_{k-\kappa} - \gamma_\kappa\, \gamma_{k-\kappa} - a_\kappa\, \gamma_{k-\kappa} + \gamma_\kappa\, a_{k-\kappa}).$$

But

$$\sum_{-\infty}^{\infty} a_\kappa\, a_{k-\kappa} = \tfrac{1}{2}\sum_{-\infty}^{\infty} (a_\kappa\, a_{k-\kappa} + a_{k-\kappa}\, a_\kappa) = 0$$

$$\sum_{-\infty}^{\infty} \gamma_\kappa \gamma_{k-\kappa} = \tfrac{1}{2} \sum_{-\infty}^{\infty} (\gamma_\kappa \gamma_{k-\kappa} + \gamma_{k-\kappa} \gamma_\kappa) = 0$$

and $$\sum_{-\infty}^{\infty} \gamma_\kappa a_{k-\kappa} = -\sum_{-\infty}^{\infty} a_{k-\kappa} \gamma_\kappa = -\sum_{-\infty}^{\infty} a_{k+\kappa} \gamma_{-\kappa} = -\sum_{-\infty}^{\infty} a_\kappa \gamma_{k-\kappa}.$$

Thus we get

(36) $$\boxed{b_k = -\frac{1}{\sqrt{|k|}} \sum_{-\infty}^{\infty} a_\kappa \gamma_{k-\kappa}}$$

or

(37) $$\boxed{b_k = -\frac{1}{\sqrt{|k|}} \sum_{-\infty}^{\infty} a_\kappa a^+{}_{\kappa-k}}$$

A third expression given by Jordan is gained by splitting the above sum into terms with only positive indices:

(38) $$\boxed{b_k = -\frac{1}{\sqrt{|k|}} \left\{ \sum_{\kappa=\frac{1}{2}}^{k-\frac{1}{2}} a_\kappa \gamma_{k-\kappa} + \sum_{\kappa=\frac{1}{2}}^{\infty} (a_{k+\kappa} a_\kappa{}^+ - \gamma_{k+\kappa} \gamma_\kappa{}^+) \right\}}$$

10. The Operator B and its Commutation Properties with b_k.

The operator B is defined by Kronig as

(39) $$\mathrm{B} = i \sum_{-\infty}^{\infty} a_l c_{-l}$$

and by Jordan as

(40) $$\begin{aligned} \mathrm{B} &= \sum_{\frac{1}{2}}^{\infty} (\mathrm{N}_\kappa{}^{(+)} - \mathrm{N}_\kappa{}^{(-)}) \\ &= \sum_{\frac{1}{2}}^{\infty} (a_\kappa{}^+ a_\kappa - \gamma_\kappa{}^+ \gamma_\kappa). \end{aligned}$$

The two definitions can be shown to be equivalent if we transform a's and c's to α's and γ's and by using the commutation rules. The first definition in (40) shows immediately (as pointed out by Jordan) that B has whole number eigenvalues $0, \pm 1, \pm 2, \ldots, \ldots$.

Kronig has shown that B commutes with all b_k defined in (25). We simply reproduce his proof.

$$\mathrm{B} b_k = -\frac{1}{\sqrt{|k|}} \sum_{\substack{l,\, m \\ -\infty}}^{\infty} a_l c_{-l} a_m c_{k-m},$$

$$\mathrm{B}b_k - b_k\mathrm{B} = \frac{1}{\sqrt{|k|}} \sum_{\substack{l,m \\ -\infty}}^{\infty} (a_m c_{k-m} a_l c_{-l} - a_l c_{-l} a_m c_{k-m})$$

$$= \frac{1}{\sqrt{|k|}} \sum_{\substack{l \\ -\infty}}^{\infty} (a_l a_{k-l} + c_{-l} c_{k+l}) = 0, \tag{41}$$

using the commutation rules for a's and c's.

11. Photons.

It is known that the photons in a Hohlraum can be represented by a set of variables b_k which satisfy commutation rules of the type (35). In the case of a one-dimensional Hohlraum the light wave could be represented by a wave function

$$\psi(t - x/c) = \sum_{k=-\infty}^{\infty} b_k e^{2\pi i \nu_1 k(t-x/c)} = \phi^+. \tag{42}$$

In 3-dimensions there are some geometrical complications arising from the polarisation of light which do not affect the use of the variables* b_k but we do not treat these questions here.

Before Jordan's work it was generally believed that there were two fundamental statistics, the Fermi-Dirac statistics and the Bose-Einstein statistics. The former is connected with wave functions anti-symmetric in the particles of the assembly, the latter with symmetric wave functions. *Jordan's mathematical results can be interpreted as the fundamental physical statement that the only primary statistics is the Fermi-Dirac one with anti-symmetric wave functions.* If applied to processes in empty space, this leads to the idea that photons (as primary Bose-Einstein particles) do not exist at all, but that they are only a secondary effect appearing under special circumstances. The phenomena in empty space have really to be described by moving neutrinos and anti-neutrinos (or the corresponding waves). The phenomena attributed usually to photons are, according to Jordan, really simultaneous actions of pairs of neutrinos and anti-neutrinos. The exact formulation of these actions follows from the formulæ (25).

For a state with given numbers of neutrinos $N^{(+)}$ and $N^{(-)}$, the operator representing the *number of photons* in the kth state.

$$\mathrm{P}_k = b_k^+ b_k = b_{-k} b_k, \tag{43}$$

is in general not a diagonal matrix, *i.e.*, the number of photons has not definite values. But we can calculate its average or expectation value—the diagonal element of P_k:

$$\overline{\mathrm{P}}_k (t_{1/2}, t_{-1/2}, t_{3/2}, t_{-3/2}, \cdots\cdots, \cdots\cdots)$$

* P. A. M. Dirac, *Quantum Mechanics*, 1935, p. 229.

$$(44) \quad = \sum_{t'_{1/2}, t'_{-1/2}, t'_{3/2}, t'_{-3/2}, \cdots} | b_k (t'_{1/2}, t'_{-1/2}, t'_{3/2}, t'_{-3/2}, \cdots ; t_{1/2}, t_{-1/2}, t_{3/2}, t_{-3/2}, \cdots) |^2.$$

We observe that each a_κ has only one non-vanishing element ± 1, when t'_κ makes the jump $0 \to 1$ and when all the other t's remain unchanged ; a_κ^+ behaves in the same fashion except that the jump for t'_κ would be $1 \to 0$. The γ_κ behaves just in a similar way round as indicated in the scheme (14). Therefore $a_\kappa \gamma_{k-\kappa}$ for $\frac{1}{2} \leqslant \kappa \leqslant k - \frac{1}{2}$ has only one non-vanishing element ± 1 for $t_\kappa : 0 \to 1$ and $t_{\kappa-k} : 0 \to 1$

One term of the first sum is consequently

$$N_\kappa^{(+)} N_{k-\kappa}^{(-)}.$$

In the same way the terms of the other sums are

$$N_{k+\kappa}^{(+)} (1 - N_\kappa^{(+)}) \text{ and } N_{k+\kappa}^{(-)} (1 - N_\kappa^{(-)}).$$

The result is :

$$(45) \quad \overline{P_k} = \frac{1}{k} \sum_{\kappa = \frac{1}{2}}^{k - \frac{1}{2}} N_\kappa^{(+)} N_{k-\kappa}^{(-)} + \frac{1}{k} \sum_{\kappa = \frac{1}{2}}^{\infty} \{N_{k+\kappa}^{(+)} (1 - N_\kappa^{(+)}) + N_{k+\kappa}^{(-)} (1 - N_\kappa^{(-)})\}.$$

Jordan interprets this formula in the following way : There are two kinds of interaction of neutrinos and matter which are equivalent to an interaction of photons with matter :

(1) *Simultaneous absorption of a neutrino and an anti-neutrino whose total energy is equal to that of the energy change of the atom* : $\kappa + (k - \kappa) = k$ *(usually ascribed to the absorption of one photon).*

(2) *Raman effect of neutrinos or anti-neutrinos* : *One neutrino (anti-neutrino) of the energy* $k + \kappa$ *is absorbed, another of the same kind of the energy* κ *is emitted.*

The processes (1) *and* (2) *are* not *essentially different, if we use the idea of only one kind of neutrinos having positive and negative energy states* ; the process (1) could be considered also as a Raman effect where a neutrino of positive energy is absorbed and one of negative energy is emitted. This is mathematically represented directly by the short formula (37).

12. Statistical Equilibrium.

The most important result of Jordan is the proof that this new conception of radiation leads to the correct results for the statistical equilibrium, *i.e.*, Planck's law.

We have two kinds of neutrinos satisfying the Fermi-Dirac statistics. The well-known formula for the entropy of an assembly of $N_l^{(+)}$ neutrinos and $N_l^{(-)}$ anti-neutrinos of nearly equal energy $\bar{l}$ (in units $h\nu_1$) is

$$(46)\quad S = -k \sum_{\mu} \begin{Bmatrix} (1-N_{\mu}^{(+)}) \log (1-N_{\mu}^{(+)}) + N_{\mu}^{(+)} \log N_{\mu}^{(+)} \\ + (1-N_{\mu}^{(-)}) \log (1-N_{\mu}^{(-)}) + N_{\mu}^{(-)} \log N_{\mu}^{(-)} \end{Bmatrix},$$

k being the Boltzmann constant.

Since the anti-neutrinos correspond to holes in the multitude of neutrinos with negative energy, a neutrino can disappear only by falling in a hole, or by a simultaneous disappearance of an anti-neutrino. Therefore

$$(47)\quad \sum_{\mu} (N_{\mu}^{(+)} - N_{\mu}^{(-)}) = B,$$

is constant. Besides we have the total energy given as

$$(48)\quad \sum_{\mu} \mu (N_{\mu}^{(+)} + N_{\mu}^{(-)}) = \frac{E}{h\nu_1}.$$

Using two multipliers which we call $\psi\beta$ and β, we get by the variation of S given by (46) under the two conditions (47) and (48)

$$\log \frac{1 - N_l^{(+)}}{N_l^{(+)}} = \beta (l + \psi),$$

$$\log \frac{1 - N_l^{(-)}}{N_l^{(-)}} = \beta (l - \psi).$$

From this we find the Fermi distribution law

$$(49)\quad N_l^{(+)} = \frac{1}{e^{\beta(l+\psi)} + 1}, \quad N_l^{(-)} = \frac{1}{e^{\beta(l-\psi)} + 1}$$

or if we introduce the notations

$$y = e^{-\beta l} \quad \text{and} \quad a = e^{-\beta\psi},$$

$$(50)\quad N_l^{(+)} = \frac{a\,y}{1+a\,y} \text{ and } N_l^{(-)} = \frac{\frac{y}{a}}{1+\frac{y}{a}}.$$

Introducing these into the expression of the entropy and applying the second law of thermodynamics it is shown in the well-known manner that $\beta = h\nu_1/kT$. We substitute these expressions (50) in Jordan's formula (45),

$$\overline{P_l} = \frac{1}{l} \sum_{\kappa=\frac{1}{2}}^{l-\frac{1}{2}} N_{\kappa}^{(+)} N_{l-\kappa}^{(-)} + \frac{1}{l} \sum_{\kappa=\frac{1}{2}}^{\infty} \{N_{l+\kappa}^{(+)} (1-N_{\kappa}^{(+)}) + N_{l+\kappa}^{(-)} (1-N_{\kappa}^{(-)})\}.$$

Denoting

$$\frac{\kappa}{l} = \omega,$$

we have

$$e^{-\beta\kappa} = y^{\kappa\omega}$$

and $d\kappa = l\,d\omega$, $\nu_1\, l = \nu$.

We replace the sum by integrals* and get

$$(51)\quad \bar{P}(\nu) = \int_0^1 \frac{ay^{\omega}}{1+ay^{\omega}} \cdot \frac{\frac{1}{a}y^{1-\omega}}{1+\frac{1}{a}y^{1-\omega}}\, d\omega + \int_0^{\infty} \left\{ \frac{ay^{1+\omega}}{1+ay^{1+\omega}} \cdot \frac{1}{1+ay^{\omega}} + \frac{\frac{1}{a}y^{1+\omega}}{1+\frac{1}{a}y^{1+\omega}} \cdot \frac{1}{1+\frac{1}{a}y^{\omega}} \right\} d\omega.$$

The first we write

$$\int_0^1 \frac{y\,d\omega}{(1+ay^{\omega})\,(1+\frac{1}{a}y^{1-\omega})} = \int_0^{\infty} - \int_1^{\infty},$$

which by changing in the second integral ω to $1 + \omega$ becomes

$$y\int_0^{\infty} \left\{ \frac{1}{(1+ay^{\omega})\,(1+\frac{1}{a}y^{1-\omega})} - \frac{1}{(1+ay^{1+\omega})\,(1+\frac{1}{a}y^{-\omega})} \right\} d\omega.$$

The second integral here cancels the first part of the remaining integral in (51) so that

$$\bar{P}(\nu) = y\int_0^{\infty} \left\{ \frac{1}{(1+ay^{\omega})\,(1+\frac{1}{a}y^{1-\omega})} + \frac{\frac{1}{a}y^{1+\omega}}{(1+\frac{1}{a}y^{1+\omega})\,(1+\frac{1}{a}y^{\omega})} \right\} d\omega$$

$$= y\int_0^{\infty} \left\{ \frac{ay^{\omega-1}}{(1+ay^{\omega})\,(1+ay^{\omega-1})} + \frac{ay^{-\omega-1}}{(1+ay^{-\omega})\,(1+ay^{-\omega-1})} \right\} d\omega$$

$$= \int_{-\infty}^{\infty} \frac{ay^{\omega}}{(1+ay^{\omega})\,(1+ay^{\omega-1})}\, d\omega.$$

We write the above formula as

$$(52)\quad \bar{P}(\nu) = \int_{-\infty}^{\infty} \frac{ay^{\omega}}{1+ay^{\omega}} \left(1 - \frac{ay^{\omega-1}}{1+ay^{\omega-1}}\right) d\omega$$

$$(53)\quad = \boxed{\frac{1}{l} \sum_{\kappa=-\infty}^{\infty} N_{\kappa}\,(1 - N_{\kappa-l})}$$

---

* One can also readily evaluate these integrals by substituting $\frac{1-z}{z}$ for ay^{ω} in the first integral and $\frac{1-z}{z}$ for $ay^{1+\omega}$ and $\frac{1-z}{z}$ for $\frac{1}{a}y^{1+\omega}$ in the other integrals.

We can interpret this formula by assuming only one kind of neutrinos with the number N_κ *in the state* κ *where* κ *may be positive or negative.* Then the formula gives the average photon density of energy l as a *Raman effect* with the universal rule: absorption of a neutrino of any (positive or negative) energy κ and simultaneous emission of a neutrino with the energy $\kappa - l$. We mention this to confirm our idea that the introduction of a spin of the neutrino by Jordan is quite unnecessary.

Since $y < 1$ we can substitute

$$ay^\omega = \frac{1-z}{z},$$

so that $ay^\omega \, d\omega = -\frac{1}{z^2 \log y}\, dz.$

Then

$$\overline{P(\nu)} = -\int_0^1 \frac{1}{\log y} \cdot \frac{dz}{z^2\left(1+\frac{1-z}{z}\right)\left(1+\frac{1}{y}\frac{1-z}{z}\right)} = -\frac{y}{\log y}\int_0^1 \frac{dz}{1+(y-1)z}.$$

$$= -\frac{y}{\log y}\left[\frac{\log(1+y-1\,z)}{y-1}\right]_0^1 = \frac{y}{1-y}.$$

Introducing here the value of y, we get

$$(54)\quad \overline{P(\nu)} = \frac{e^{-\frac{h\nu}{kT}}}{1-e^{-\frac{h\nu}{kT}}} = \frac{1}{e^{\frac{h\nu}{kT}}-1}.$$

This is the well-known expression for the photon density which by multiplication with the number of photons in the interval $d\nu$ leads to Planck's formula of radiation.

13. Relation between the Energy of Neutrinos and Photons.

We have already remarked that a neutrino field with definite numbers of neutrinos of both kinds, $N_\kappa^{(+)}$, $N_\kappa^{(-)}$ is in general not equivalent to a photon field of a given number of photons, P_k. In the language of quantum mechanics we can understand this in the following way. There is a Hilbert space representing all the states of the field. If we choose a co-ordinate system in which the quantities $N_\kappa^{(+)}$, $N_\kappa^{(-)}$ are all represented by diagonal matrices, the quantities P_k are not so. But there will be another co-ordinate system where P_k's are diagonal; we will then have a pure photon state. The question is to form an idea as to the relation of these different states.

For this purpose we prove an identity derived first by de Kronig connecting the total energy of the neutrinos with that of the photons. The energy of the neutrinos is

$$(55)\quad \mathrm{E} = \sum_{n=\frac{1}{2}}^{\infty} n\,(\mathrm{I}_n + \mathrm{N}_n) = \sum_{n=\frac{1}{2}}^{\infty} n\,(\mathrm{N}_n^{(+)} + \mathrm{N}_n^{(-)}).$$

The energy of the photons is

$$(56)\quad \mathrm{W} = \sum_{n=1}^{\infty} n\,\mathrm{P}_n$$

The proposition is

$$(57)\quad \boxed{\mathrm{E} - \mathrm{W} = \tfrac{1}{2}\,\mathrm{B}^2}\,,$$

where B is the quantity defined in (39) which, as we have shown, commutes with all the b_k. Kronig's proof of the proposition is as follows:

$$\mathrm{W} = \sum_{1}^{\infty} k\,\mathrm{P}_k = \sum_{1}^{\infty} k\,b_k^{+}\,b_k$$

$$= -\sum_{\substack{l,\,m\\-\infty}}^{\infty} \sum_{k=1}^{\infty} a_l\,c_{-k-l}\,a_m\,c_{k-m}$$

$$(58)\quad = \sum_{\substack{l,\,m\\-\infty}}^{\infty\prime} \sum_{k=1}^{\infty} a_l\,a_m\,c_{-k-l}\,c_{k-m} + \sum_{l=-\infty}^{\infty} \sum_{k=1}^{\infty} a_l\,a_{-l}\,c_{-k-l}\,c_{k+l},$$

where the dash over the summation sign indicates that $l \neq -m$. Changing k to $-k$, l to m, m to l in the first part of (58) and using the commutation laws, we get

$$(59)\quad \mathrm{W} = \sum_{\substack{l,\,m\\-\infty}}^{\infty\prime} \sum_{k=-1}^{-\infty} a_l\,a_m\,c_{-k-l}\,c_{k-m} + \sum_{l=-\infty}^{\infty} \sum_{k=1}^{\infty} a_l\,a_{-l}\,c_{-k-l}\,c_{k+l}.$$

From (39) we see that

$$(60)\quad \mathrm{B}^2 = \sum_{\substack{l,\,m\\-\infty}}^{\infty\prime} a_l\,a_m\,c_{-l}\,c_{-m} + \sum_{l=-\infty}^{\infty} a_l\,a_{-l}\,c_{-l}\,c_l \quad .$$

We first observe that

$$(61)\quad \sum_{\substack{l,\,m\\-\infty}}^{\infty\prime} \sum_{k=-\infty}^{\infty} a_l\,a_m\,c_{-k-l}\,c_{k-m} = \sum_{\substack{l,\,m\\-\infty}}^{\infty\prime} a_l\,a_m \sum_{k=-\infty}^{\infty} c_{-k-l}\,c_{k-m} = 0,$$

using the commutation rules for c's. Thus adding (58), (59) and (60) and using (61), we get

$$2\,\mathrm{W} + \mathrm{B}^2 = 2 \sum_{l=-\infty}^{\infty} a_l\,a_{-l} \sum_{k=1}^{\infty} c_{-k-l}\,c_{k+l} + \sum_{-\infty}^{\infty} a_l\,a_{-l}\,c_{-l}\,c_l.$$

We split the summations in a manner such that each summation index so that k or l assumes only positive values.

$$2\,W + B^2 = 2\sum_{l=\frac{1}{2}}^{\infty} a_l\, a_{-l} \sum_{k=1}^{\infty} c_{-k-l}\, c_{k+l} + 2\sum_{l=3/2}^{\infty} a_{-l}\, a_l \sum_{k=1}^{l-\frac{1}{2}} c_{-k+l}\, c_{k-l}$$

$$+ 2\sum_{l=3/2}^{\infty} a_{-l}\, a_l \sum_{k=l+\frac{1}{2}}^{\infty} c_{-k+l}\, c_{k-l} + 2\, a_{-\frac{1}{2}}\, a_{\frac{1}{2}} \sum_{1}^{\infty} c_{-k+\frac{1}{2}}\, c_{k-\frac{1}{2}}$$

$$+ \sum_{l=\frac{1}{2}}^{\infty} a_l\, a_{-l}\, c_{-l}\, c_l + \sum_{l=\frac{1}{2}}^{\infty} a_{-l}\, a_l\, c_l\, c_{-l}$$

$$= 2\sum_{l=\frac{1}{2}}^{\infty} (1 - L_l) \sum_{k=1}^{\infty} N_{k+l} + \sum_{l=3/2}^{\infty} L_l \sum_{k=1}^{l-\frac{1}{2}} (1 - N_{-k+l})$$

$$+ 2\sum_{l=3/2}^{\infty} L_l \sum_{k=l+\frac{1}{2}}^{\infty} N_{k-l} + 2\, L_{\frac{1}{2}} \sum_{k=1}^{\infty} N_{k-\frac{1}{2}}$$

$$+ \sum_{l=\frac{1}{2}}^{\infty} (1 - L_l)\, N_l + \sum_{l=\frac{1}{2}}^{\infty} L_l\, (1 - N_l)$$

$$= 2\sum_{l=\frac{1}{2}}^{\infty} (1 - L_l) \sum_{j=l+1}^{\infty} N_j + 2\sum_{l=3/2}^{\infty} L_l \sum_{j=\frac{1}{2}}^{l-1} (1 - N_j)$$

$$+ 2\sum_{l=3/2}^{\infty} L_l \sum_{k=\frac{1}{2}}^{\infty} N_j$$

$$+ 2\, L_{\frac{1}{2}} \sum_{k=1}^{\infty} N_{k-\frac{1}{2}} + \sum_{l=\frac{1}{2}}^{\infty} (1 - L_l)\, N_l + \sum_{l=\frac{1}{2}}^{\infty} L_l\, (1 - N_l)$$

$$= (L_{\frac{1}{2}} + N_{\frac{1}{2}}) + 2\sum_{l=3/2}^{\infty} \sum_{j=l+1}^{\infty} N_j + 2\sum_{l=3/2}^{\infty} L_l \sum_{j=\frac{1}{2}}^{l-1} 1$$

$$+ 3\sum_{3/2}^{\infty} N_j + \sum_{3/2}^{\infty} L_j$$

$$= (L_{\frac{1}{2}} + N_{\frac{1}{2}}) + 2\sum_{3/2}^{\infty} (l - \tfrac{3}{2})\, N_l + 2\sum_{3/2}^{\infty} (l - \tfrac{1}{2})\, L_l + 3\sum_{3/2}^{\infty} N_l + \sum_{3/2}^{\infty} L_l$$

$$= 2\sum_{l=\frac{1}{2}}^{\infty} l\, (L_l + N_l) = 2\,E.$$

Thus

$$2\,W + B^2 = 2\,E \tag{62}$$

or

$$\boxed{E - W = B^2/2}$$

Now we can answer the question put forward in the beginning of this section.

The necessary and sufficient condition that the whole neutrino energy appears in the form of photon energy is $B = 0$ or $N^{(+)} = N^{(-)}$. These states are called pure photon states or pure light fields.

The other extreme case is a pure neutrino field if $W = 0$ and $E = B^2/2$.

There are innumerable cases intermediate between these pure fields. As we have shown in (41) that B commutes with all b_k, the matrices representing b_k are reducible; they split up into finite parts corresponding to the eigenvalues $0, \pm 1, \pm 2, \ldots$, of B. For, we can take a matrix representation where B is diagonal; if r and s symbolise states of the neutrinos, then

$$B(r, s) = B(r)\delta(r, s).$$

The commutability

$$B\, b_k = b_k\, B$$

gives in this representation

$$B(r)\, \delta(r, t)\, b_k(t, s) = b_k(r, t)\, B(t)\, \delta(t, s),$$

or $$B(r)\, b_k(r, s) = b_k(r, s)\, B(s),$$

from which we conclude that $b_k(r, s) = 0$ for each pair of states which do not belong to the same eigenvalue of B, $B(r) \neq B(s)$. Therefore all impure fields can be classified with 0, or 1, or 2, ... not compensated neutrinos (or anti-neutrinos); Jordan calls this number the *resultant neutrino charge.*

14. Conclusion.

The standpoint assumed by Jordan is the following. Before the radioactive processes revealed the probability of the existence of the neutrinos, the only experimentally known wave fields were those which appear now as pure light fields. They turn out to be only a limiting case of a very much larger multitude of possible fields, which contain free (not compensated) neutrinos. The validity of this hypothesis could be experimentally tested by a study of a possible influence of radiation fields on the β-decay. If it is true that the β-emission is accompanied by an emission of a neutrino there should be an influence of an external neutrino field on the β-emission. But since light fields are nothing than neutrino fields (with neutrino pairs) we should also expect an influence of light radiation on the β-decay. The law of this interaction has yet to be calculated.

We wish to make another remark. Quantum mechanics was started by replacing the Fourier amplitudes $q_k e^{2\pi i \nu_0 kt}$ of co-ordinate function $q(t)$ by matrix elements with two indices $q_{kl} e^{2\pi i \nu_{kl} t}$. In analogy, one could expect that in a quantum field theory the Fourier elements $q_k e^{2\pi i \nu_0 k(t-x/c)}$ of a quantity representing a progressive wave $q(t - x/c)$ should be replaced by matrix elements $q_{kl} e^{2\pi i \nu_{kl}(t-x/c)}$. Here, as in quantum

mechanics, one should expect the combination law $\nu_{kl} + \nu_{lm} = \nu_{km}$. In the previous theories of radiation fields, there was no indication that something like that would lead to a deeper understanding. But here, in Jordan's neutrino theory, we have for the photon amplitudes the expression

$$\frac{\sqrt{|k|}}{i}\, b_k = \sum_{l=-\infty}^{\infty} a_l\, c_{k-l}, \tag{63}$$

where the right-hand sum is apparently the coefficient of the two Fourier series with the coefficients a_k, c_k. Now it suggests itself that we have really to do with matrices and their multiplication: a_{kl}, c_{kl} and

$$\boxed{\sum_{n=-\infty}^{\infty} a_{kn}\, c_{nl}} \tag{64}$$

where each element of these matrices is again a matrix or more generally a non-commuting quantity of the kind treated here. It seems to be attractive to follow this indication.

During writing this article, we have received the manuscript of a new article* of Jordan and de Kronig in which they treat the 3-dimensional case. There appear no new fundamental difficulties, but there are some interesting features which are beyond the scope of this article to be reported. Also in this paper, Jordan and Kronig have not changed their standpoint to consider the distinction between the neutrino and the anti-neutrino as the value of the spin instead of states and holes as we do here.

* We are very grateful for having had the privilege of knowing about this work before publication.

ON THE ERROR TERM IN A CERTAIN SUM.

By M. L. N. Sarma, B.A. (Hons.)

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(Communicated by Dr. S. Chowla.)

Let $\phi(n)$ denote the number of positive integers not exceeding n and prime to it. It is known that if

$$\sum_{n=1}^{x} \phi(n) - \frac{3}{\pi^2} x^2 = \mathrm{E}(x),$$

then[1]

(1) $\quad \mathrm{E}(x) = \mathrm{O}(x \log x),$

(2) $\quad \mathrm{E}(x) = \Omega(x \log\log\log x),$

(3) $\quad \sum_{x=1}^{\mathrm{R}} \mathrm{E}(x) \sim \frac{3}{2\pi^2} \mathrm{R}^2.$

The object of this note is to refute the conjecture that

(?) $\mathrm{E}(1), \mathrm{E}(2), \mathrm{E}(3)$, *etc., are all positive.* In fact calculation shows that *the least integral value of* m *for which* $\mathrm{E}(\mathrm{m}) < 0$ *is* $\mathrm{m} = 820$.

The following is a table of values of $\sum_{1}^{x} \phi(n)$ and of $\mathrm{E}(x)$ for different values of x. We write

$$\Phi(x) = \sum_{n=1}^{x} \phi(n).$$

x	$\Phi(x)$	$\mathrm{E}(x)$
300	27398	41·27
350	37330	94·45
400	48678	43·81
450	61634	81·35
500	76116	125·08
550	92022	72·98
600	109500	73·07
650	128602	177·34
700	149018	75·79
750	171018	38·43
800	194750	213·24
820	204376	− 9·18

For $821 \leqslant m$ (integral) $\leqslant 1000$ we find that $\mathrm{E}(m)$ is positive again.

[1] For (1) see Landau's "*Handbuch der .... Primzahlen* II". (2), (3) and the conjecture (?) are due to Chowla and Pillai. See *Journ. London Math. Soc.*, 1930, 5, 95-101.

Note: J. J. Sylvester, Collected Mathematical Papers, Vol. IV, 101-109 (1912), tabulates $\phi(n)$, $\Phi(n)$, and $\frac{3}{\pi^2}n^2$ for $n=1,2,3,\ldots,1000$. His results agree with those above. He failed to notice that $E(820)<0$.

PILLAI'S EXACT FORMULA FOR THE NUMBER $g(n)$ IN WARING'S PROBLEM.

By S. Chowla,
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§1. Let $g(n\,;\,\beta_1,\,\beta_2)$ denote the number

$$\text{Max}\quad g(n,\,m)$$
$$\beta_1 \leqslant m \leqslant \beta_2$$

where $g(n,\,m)$ is the least value of s such that m can be expressed as a sum of s nth. powers $\geqslant 0$. Thus $g(n\,;\,1,\,\infty) = g(n)$.

Let $3^n = l.\,2^n + r\ (0 < r < 2^n)$, so that r depends only on n. Pillai has shown that[1]

Theorem 1. *If* $n > n_0$, *and*

$$(1)\quad \left(\tfrac{4}{3}\right)^n + 2\left(\tfrac{5}{4}\right)^n \leqslant r \leqslant 2^n - \left(\tfrac{3}{2}\right)^n - \left(\tfrac{4}{3}\right)^n - 2\left(\tfrac{5}{4}\right)^n,$$

then $\quad g(n\,;\,1,\,\beta) = 2^n + l - 2$

where $\quad \beta = n^{5n^{11}}$.

This is his lemma 15, and a slightly modified proof has been published by Padhy.[2] Pillai proceeds to prove by the Vinogradow method (*Annals of Mathematics*, May 1935) that

Theorem 2. *If* $n > n_0$ *then*

$$g(n\,;\,\beta,\,\infty) \leqslant 2n^9,$$

where $\quad \beta = n^{5n^{11}}$.

It is an immediate consequence of these two theorems that

Theorem 3. *If* r *satisfies* (1) *above, then, for* $n > n_0$,

$$g(n) = 2^n + l - 2.$$

In this note we prove that

Theorem 4. (1) *is true for infinitely many* n.

This is obviously a consequence of

Theorem 5. *Let* $f(n)$ *denote the fractional part of* $\left(\tfrac{3}{2}\right)^n$. *Then the inequality*

$$\tfrac{1}{8} \leqslant f(n) \leqslant \tfrac{5}{8}$$

is true for infinitely many n.

From theorems 4 (or 5) and 3 we obtain

Theorem 6. *Pillai's exact formula for* $g(n)$, *namely*

$$g(n) = 2^n + l - 2.$$

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[1] *Annamalai University Journal*, March 1936, **5**, No. 2.

[2] See the paper which follows this.

is true for infinitely many n.

§2. Write $(\frac{3}{2})^n = l_n + f(n)$, so that l_n is an integer.

Lemma 1. *If* $0 < f(m) < \frac{1}{6}$, *then, either*

$$\text{(i) } \tfrac{1}{6} \leqslant f(m+1) \leqslant \tfrac{3}{4}$$

or $$\text{(ii) } f(m+1) = \tfrac{3}{2} f(m),\ f(m+1) < \tfrac{1}{6}.$$

Proof.—We have

$$(\tfrac{3}{2})^m = l_m + f(m),\ 0 < f(m) < \tfrac{1}{6}.$$

If $l_m \equiv 1\ (2)$ it follows that

$$\tfrac{1}{6} < f(m+1) = \tfrac{1}{2} + \tfrac{3}{2} f(m) < \tfrac{3}{4},$$

and thus (i) holds.

If, however, $l_m \equiv 0\ (2)$, we obtain

$$(2)\quad f(m+1) = \tfrac{3}{2} f(m) \leqslant \tfrac{1}{6} \cdot \tfrac{3}{2} = \tfrac{1}{4}$$

From (2), either

$$(\alpha)\quad f(m+1) = \tfrac{3}{2} f(m) \text{ and } \tfrac{1}{6} \leqslant f(m+1) \leqslant \tfrac{1}{4}$$

or

$$(\beta)\quad f(m+1) = \tfrac{3}{2} f(m) \text{ and } f(m+1) < \tfrac{1}{6}.$$

In case (α), (i) holds. Case (β) is (ii). Hence the lemma.

Repeated application of lemma 1 gives the generalized

Lemma 2. *If* $f(m+r) < \frac{1}{6}$ $[r = 0, 1, 2, \cdots, s-1]$ *then, either,*

$$\text{(i) } \tfrac{1}{6} \leqslant f(m+s) \leqslant \tfrac{3}{4}$$

or

$$\text{(ii) } f(m+s) = (\tfrac{3}{2})^s f(m),\ f(m+s) < \tfrac{1}{6}.$$

An exactly similar reasoning proves that—writing $\theta(m)$ for $1 - f(m)$,

Lemma 3. *Lemma* 2 *is true when* $f(m)$ *is replaced by* $\theta(m)$ *throughout.*

Since $f(m)$ is fixed, and $(\frac{3}{2})^s \to \infty$ as $s \to \infty$, (ii) of lemma 2 will be false for a certain s, and hence

Lemma 4. *If* $0 \leqslant f(m) < \frac{1}{6}$, *then there exists an integer* $s = s(m)$ *such that*

$$\tfrac{1}{6} \leqslant f(m+s) \leqslant \tfrac{3}{4}. \qquad [s > 0].$$

Similarly from lemma 3 we get lemma 4 with the function $f(m)$ replaced by $\theta(m)$, which means that, since $\theta(m) = 1 - f(m)$,

Lemma 5. *If* $f(m) > \frac{5}{6}$, *then there exists an integer* $s = s(m)$ *such that*

$$\tfrac{1}{4} \leqslant f(m+s) \leqslant \tfrac{5}{6}. \qquad [s > 0].$$

From lemmas 4 and 5, theorem 4 is an immediate consequence.

§3. S. S. Pillai has communicated to me the more difficult result that the number of solutions of

$$f(n) \leqslant 1 - \frac{l+3}{2^n},\ 1 \leqslant n \leqslant x$$

is greater than $\frac{x}{4}$ for large x. But this result does not contain theorem 5.

PILLAI'S EXACT FORMULA FOR THE NUMBER $g(n)$ IN WARING'S PROBLEM.

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1. *Introduction.*

Let $g(n, \beta)$ denote the least value s required to represent every positive integer $\leqslant \beta$ as a sum of s non-negative nth powers. Further let $l = [(\frac{3}{2})^n]$, where $[x]$ denotes the integral part of x. Let $3^n = l2^n + r$, so that r depends only on n. S. S. Pillai has proved[1]

Theorem 1. *If* $r \leqslant 2^n - (l + 3)$, $\beta = n^{5n^{11}}$, then

$$g(n, \beta) = 2^n + l - 2$$

for $n > n_0$.

From this he deduces by Vinogradow's method a formula for $g(n)$ $\{=g(n, \infty)\}$ which is exact in most cases.[2] On account of the importance of Pillai's formula for $g(n)$ it was thought worthwhile to give a slightly simplified and more complete[3] account of the proof of Theorem 1. For the sake of simplicity I confine myself to smaller range of values of r and prove, in fact,

Theorem 2. *If* $(\frac{4}{3})^n + 2(\frac{5}{4})^n \leqslant r \leqslant 2^n - (\frac{3}{2})^n - (\frac{4}{3})^n - 2(\frac{5}{4})^n$,

then

$$g\left(n, n^{n^A}\right) = 2^n + l - 2,$$

where A is any preassigned (arbitrarily large but fixed) number, and $n > n_0$ (A).

2. *Lemmas.*

In this section I give an account of Pillai's lemmas. Let $v = \frac{1}{n}$. An nth power must be understood to mean the nth power of an integer $\geqslant 0$.

Lemma 1.[4] If every integer M for which $f < \mathrm{M} \leqslant h$ is a sum of $(s - 1)$, nth powers, and if m is the highest integer such that

$$(m + 1)^n - m^n < h - f,$$

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[1] "On Waring's Problem," *Annamalai University Journal*, 5, No. 2. Theorem 1 is proved in lemmas 12 to 18. My thanks are due to Dr. Chowla for putting me into touch with Pillai's work.

[2] See the preceding note by S. Chowla.

[3] Pillai's proofs of certain lemmas, especially those of lemmas 16 and 17, are incomplete.

[4] This lemma is due to L. E. Dickson. The proof given here is mine own.

then every integer in the interval $[f, h + (m + 1)^n]$ is a sum of s, nth powers.

Proof. It is necessary to prove the lemma only for the interval $[h, h + (m + 1)^n]$. For the numbers M of this interval, we have

$$h - (m + 1)^n < \mathrm{M} - (m + 1)^n \leqslant h.$$

Now every M such that

$$f < \mathrm{M} - (m + 1)^n \leqslant h$$

$$i.e., \quad f + (m + 1)^n < \mathrm{M} \leqslant h + (m + 1)^n$$

is a sum of $(\overline{s - 1} + 1 =)\ s$, nth powers. So it is sufficient to prove the lemma for the interval $[h, f + (m + 1)^n]$ or for the interval $[h, h + m^n]$, since $f + (m + 1)^n < h + m^n$. Since

$$(r + 1)^n - r^n < h - f, \quad \text{for } r < m,$$

we can repeat this process (that of lessening the interval) m times and conclude at the end that the lemma is true if it is true for the interval $[h, h + 1]$. Since $(h + 1)$ is a sum of $(\overline{s - 1} + 1 =)\ s$, nth powers, the lemma is proved.

Lemma 2. If m is any positive integer $\geqslant 2$, then any integer N is expressible in the form

$$\mathrm{N} = \mathrm{M} + a,$$

where M is a sum of $\dfrac{2 \log \mathrm{N}}{\log 2}\left(\dfrac{m}{m-1}\right)^n$, nth powers and $0 \leqslant a < m^n$.

Proof. (1) Let $\mathrm{N} < 2\ m^n$. Then $\mathrm{N} = bm^n + a$, where $b \leqslant 1$ and $0 \leqslant a < m^n$.

Obviously $b \leqslant \dfrac{2 \log \mathrm{N}}{\log 2}\left(\dfrac{m}{m-1}\right)^n$, (since if $b = 1$, $\mathrm{N} > m^n$).

(2) Let $\mathrm{N} \geqslant 2\ m^n$. Put $r_0 = \mathrm{N}$.

Let $b_1 = \left[\left(\dfrac{r_0}{2}\right)^{\nu}\right]$, $r_0 = q_1\, b_1^n + r_1$, where $q_1 = \left[\left(\dfrac{r_0}{b_1^n}\right)\right]$, $r_1 < b_1^n$. Then $r_1 \leqslant \dfrac{r_0}{2}$.

Put $b_2 = \left[\left(\dfrac{r_1}{2}\right)^{\nu}\right]$, $r_1 = q_2\, b_2^n + r_2$, where $q_2 = \left[\left(\dfrac{r_2}{b_2^n}\right)\right]$, $r_2 < b_2^n$.

$$\text{So } r_2 \leqslant \frac{r_1}{2} \leqslant \frac{r_0}{2^2}.$$

Put $b_3 = \left[\left(\dfrac{r_2}{2}\right)^{\nu}\right]$ and so on.

Then $\mathrm{N} = r_0 = q_1\, b_1^n + \ldots\ldots + q_l\, b_l^n + r_l$, where $r_l \leqslant \dfrac{r_0}{2^l} = \dfrac{\mathrm{N}}{2^l}$,

$$b_l = \left[\left(\frac{r_{l-1}}{2}\right)^{\nu}\right], \quad q_l = \left[\left(\frac{r_{l-1}}{b_l^n}\right)\right].$$

Since $r_0 \geqslant 2\,m^n$, it is possible to choose l so that

$$r_{l-1} \geqslant 2\,m^n > r_l.$$

Put $r_l = bm^n + a$, where $b \leqslant 1$ and $0 \leqslant a < m^n$.

So $N = M + a$,

where M is a sum of $(q_1 + \ldots. + q_l + b)$, nth powers and $0 \leqslant a < m^n$.

Now for $k = 1, 2, \ldots., l$

$$q_k \leqslant \frac{r_{k-1}}{b_k^n} = \frac{r_{k-1}}{\left[\left(\frac{r_{k-1}}{2}\right)^\nu\right]^n} \leqslant \frac{r_{k-1}}{\left\{\left(\frac{r_{k-1}}{2}\right)^\nu - 1\right\}^n}$$

$$= \frac{2}{\left\{1 - \left(\frac{2}{r_{k-1}}\right)^\nu\right\}^n} \leqslant \frac{2}{\left\{1 - \left(\frac{2}{r_{l-1}}\right)^\nu\right\}^n}$$

since the r's form a decreasing sequence,

$$\leqslant \frac{2}{\left\{1 - \left(\frac{2}{2m^n}\right)^\nu\right\}^n} = 2\left(\frac{m}{m-1}\right)^n.$$

Also $\quad b \leqslant 1 < 2\left(\frac{m}{m-1}\right)^n.$

Hence $\quad q_1 + \ldots. + q_l + b \leqslant 2\,(l+1)\left(\frac{m}{m-1}\right)^n.$

Moreover

$$\frac{N}{2^{l-1}} \geqslant r_{l-1} \geqslant 2\,m^n, \textit{ i.e., } \frac{2N}{m^n} \geqslant 2^{l+1}.$$

Since $m \geqslant 2$ we have $N \geqslant 2^{l+1}$, *i.e.*, $l + 1 \leqslant \dfrac{\log N}{\log 2}$.

Thus the lemma is proved.

Lemma 3. If every positive integer M such that $F < M \leqslant F + 2^n$ is the sum of s, nth powers, then every positive integer in the interval (F, n^{n^4}) is the sum of

$$s + (\tfrac{3}{2})^n + (\tfrac{4}{3})^n + 2(\tfrac{5}{4})^n - 3,$$

nth powers, provided $n > n_0$ (A).

Proof. For the interval $[F, F + 2^n]$, the m of lemma 1 is unity. So every integer in the interval $[F, F + 2 \cdot 2^n]$ is a sum of $(s + 1)$, nth powers. In this way we see that every integer in the interval $[F, F + 3^n]$ is a sum of $s + (\frac{3}{2})^n$, nth powers. In fact, the same argument shows that every positive integer in the interval $[F, F + m^n]$ is a sum of

$$s + (\tfrac{3}{2})^n + (\tfrac{4}{3})^n + \ldots\ldots\ldots + \left(\frac{m}{m-1}\right)^n$$

nth powers.

Now let $F < N \leqslant n^{n^A}$. By lemma 2

$$N - F - 1 = M + a,$$

where M is a sum of $\dfrac{2 \log (N - F - 1)}{\log 2} \left(\dfrac{m}{m-1}\right)^n$ nth powers and $0 \leqslant a < m^n$.

Hence $N = M + (a + F + 1)$, and $F < (a + F + 1) \leqslant F + m^n$.

So $(a + F + 1)$ is a sum of

$$s + (\tfrac{3}{2})^n + \ldots\ldots\ldots + \left(\frac{m}{m-1}\right)^n.$$

nth powers. Hence N is a sum of

$$s + (\tfrac{3}{2})^n + \ldots\ldots + \left(\frac{m}{m-1}\right)^n + 2\,\frac{\log (N - F - 1)}{\log 2}\left(\frac{m}{m-1}\right)^n,$$

nth powers.

Since $(N - F - 1) < n^{n^A}$,

$$(\tfrac{5}{3})^n + \ldots\ldots + \left(\frac{m}{m-1}\right)^n + 2\,\frac{\log (N - F - 1)}{\log 2}\left(\frac{m}{m-1}\right)^n < (\tfrac{5}{4})^n - 3,$$

when $m = 7$ and $n > n_0$ (A).

Hence the lemma follows.

3. Proof of Theorem 2.

(1) Every positive integer $< l2^n$ is of the form $a\,2^n + b$, where $a < l$, $b < 2^n$, and so is a sum of $l - 1 + 2^n - 1$, nth powers. Hence every positive integer $\leqslant l2^n$ is a sum of $2^n + l - 2$, nth powers.

(2) Every integer x in $l2^n \leqslant x < 3^n$ is of the form $l2^n + f$, where $f < r$, and so is a sum of $l + r - 1$, nth powers.

(3) Every integer y in $3^n \leqslant y < (l + 1)\,2^n$ is of the form $3^n + \theta$, where $\theta < 2^n - r$, and so is a sum of $1 + 2^n - r - 1$, nth powers.

(4) $(l + 1)\,2^n$ is a sum of $l + 1$, nth powers.

Now $l + r - 1 \leqslant (\tfrac{3}{2})^n + 2^n - (\tfrac{3}{2})^n - (\tfrac{4}{3})^n - 2\,(\tfrac{5}{4})^n - 1 < 2^n - (\tfrac{4}{3})^n - 2\,(\tfrac{5}{4})^n$;

$$2^n - r < 2^n - (\tfrac{4}{3})^n - 2\,(\tfrac{5}{4})^n;$$

and $l + 1 \leqslant (\tfrac{3}{2})^n + 1 < 2^n - (\tfrac{4}{3})^n - 2\,(\tfrac{5}{4})^n$, for the given range of values of r.

Hence from (2), (3) and (4), every integer in the interval $[l2^n, (l + 1)\,2^n]$ is a sum of

$$2^n - (\tfrac{4}{3})^n - 2\,(\tfrac{5}{4})^n$$

nth powers, Hence, by lemma 3, every integer in the interval $[l2^n,\ n^{n^A}]$ is a sum of

$$2^n + (\tfrac{3}{2})^n - 3 \leqslant 2^n + l - 2$$

nth powers.

From (1) and above we notice that every integer $\leqslant n^{n^A}$ is a sum of 2^n+l-2, nth powers. The number $l2^n - 1$ requires exactly $2^n + l - 2$, nth powers. Hence

$$g(n, n^{n^A}) = 2^n + l - 2$$

for $n > n_0$ (A).

Pillai proceeds to show by Vinogradow's method that every integer $\geqslant \beta = n^{5n^{11}}$ needs at most $2n^9$, nth powers for $n > n_0$. Hence by Theorem 2 every integer needs

$$\text{Max } (2 + l - 2,\ 2n^9) = 2^n + l - 2$$

nth powers for $n > n_0$ and

$$(\tfrac{4}{3})^n + 2(\tfrac{5}{4})^n \leqslant r \leqslant 2^n - (\tfrac{3}{2})^n - (\tfrac{4}{3})^n - 2(\tfrac{5}{4})^n.$$

ON THE BAND SYSTEMS AND STRUCTURE OF SiF.

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Introduction.

In the course of an enquiry on the dissociation energies of certain molecules we came to deal with the SiF molecule whose spectrum has been investigated by Johnson and Jenkins.[1] Reference to this work showed that the nature of the electronic levels was left undecided and this is not surprising, since the work was done when the theory of band spectra was yet in the making. Johnson and Jenkins found a large number of bands, which on account of their appearance were divided into five groups, the so-called α, β, γ, δ and ϵ bands. They were further able to propose a vibrational analysis of the α- and β-bands, which showed, that these two systems involve a common final level, which being the lowest was regarded as the ground state of the molecule. This ground-level appears to have been regarded in literature as a $^2\Sigma$ level. Theoretical considerations which have been developed in recent years, we mean for instance the basic idea of the method of molecular orbitals of building up the configuration of the molecule by putting in electrons step by step in their energetical order, indicate, that the ground-level of the molecule SiF should rather be a $^2\Pi$ level. In view of this and the fact that the whole of the spectrum has not been systematised, we undertook a new vibrational analysis of these bands. It was not thought necessary to repeat the experiments, because of the accurate and careful data of Johnson and Jenkins. Further, the excellent reproductions of the bands, which they have published served us as well as original plates. We have been able to show that the analysis of the β-bands proposed by these authors happens to be numerically roughly correct, but the transition involved is $^2\Sigma \rightarrow {}^2\Pi$. The analysis of the α-bands, however, needs considerable revision and shows that they should be regarded as a $^2\Pi \rightarrow {}^2\Pi$ transition. The γ-bands which could not be analysed before

[1] R. C. Johnson and H. G. Jenkins, *P. R. S.*, 1927, **116(A)**, 327.

TABLE I.

Analysis of β-Bands.

v' \ v''	0	1	2	3	4	5	6
0	P 34539·3 (10)	33693·7 (10)	32859·3 (4)	32030·7 (2)	31210·8 (0)		
	Q 555·7 (10)	708·4 (10)	870·1 (5)	043·1 (2)	..		
	P 701·8 (4)	856·1 (10)	33021·0 (3)	193·7 (0)	380·2 (0)		
	Q 716·6 (9)	869·3 (10)	031·9 (6)	(212·4) (2)	..		
1	35539·0 (8)	..	..	..	32212·4 (2)	..	
	557·5 (8)	..	..	*c* 33043·9 (6)	*a* 224·8 (2)	31411·1 (0)	
	703·8 (8)	*c* 34858·5 (2)	34019·8 (7)	193·0 (3)	376·2 (1)	..	
	719·1 (7)	*c* 871·9 (2)	032·3 (8)	204·1 (5)	*c* 391·9 (2)	578·5 (0)	
2	*c* 36532·2 (2)	35085·9 (4)		..	..	..	..
	c 548·3 (3)	..		..	*c* 33217·4 (3)	*c* 32405·5 (2)	31607·4 (0)
	693·1 (3)	..		34185·1 (3)	364·8 (2)	556·4 (1)	764·1 (0)
	711·3 (2)	863·9 (5)		196·8 (4)	376·0 (4)	*c* 569·2 (2)	..
3		36666·2 (2)	35830·5 (1)	..	..	..	..
		685·2 (3)	848·5 (6)	..	..	..	..
		828·7 (3)	993·0 (2)	*vd* 35161·3 (1)	34348·3 (1)	33537·2 (0)	..
		846·4 (2)	36007·3 (2)	..	360·1 (1)	548·4 (1)	*vc* 32745 (2)
4			36801·3 (2)	35976·2 (0)	..		
			820·7 (3)	..	..		
			964·1 (2)	36138·7 (0)	*vd* 35321·6 (2)		
			982·0 (1)	*a* 153·1 (0)	..		
5				36937·3 (1)		..	
				955·9 (2)		..	
				d 37100·3 (2)		..	
				116·8 (1)		*vd* 35480·8 (1)	
6					..		
					37074·1 (1)		
					a 208·0 (0)		
					d 235·7 (0)		

are due to $^2\Sigma \rightarrow {}^2\Pi$. There is evidence to show, that the headless bands of the δ group also belong to this system. The final $^2\Pi$ level of all the three systems is the same, *i.e.*, the ground-level of the molecule. Only the bands in the ϵ system have not been classified but we have something to say about these later on. We now propose to give an account of the analysis, we have been able to make.

The β-Bands.

The analysis of this system is given in Table I. The bands form a well-defined system of close doublets in the region 3200 to 2680 A.U., and are degraded towards the shorter waves. In reality the close doublets are the P and Q heads associated with $^2\Pi_{1/2}$ and separated from a similar P and Q doublet of $^2\Pi_{3/2}$ by a frequency difference of about 161 cm.$^{-1}$ The analysis in the main yields similar constants to those given by Johnson and Jenkins because of the fact that the doublet separation is also roughly equal to the difference between the vibration frequencies of the initial and final states.[2]

The essential difference between the present analysis and the earlier one is, that whereas only two heads were ascribed to each band formerly, we now know that a $^2\Sigma \rightarrow {}^2\Pi$ transition should give rise to four heads, in this case two P and two Q heads, and these are shown in their proper places in the present analysis. This has necessitated a rearrangement of the vibrational quantum numbers used by Johnson and Jenkins and therefore a revision in the vibrational constants. Incidentally the present analysis does not indicate any pronounced perturbation, which according to the older one was present. The perturbations, if any, are only met with in the α-bands, where also it is difficult to decide this point because of the absence of Q heads, the data being obtained from R heads only. We believe that this rearrangement of the bands also removes the slight discrepancies in the isotopic obervations, mentioned by Johnson and Jenkins.

The data for the mean vibrational differences of the ground state are given in Table VII later on together with those derived for the same level from other systems. The mean vibrational differences for the initial state are : —

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[2] We cannot say anything definitely on the difficulty experienced by Johnson and Jenkins regarding the isotopic heads, because the data are not included in their paper. It is quite possible that the introduction of half quantum numbers will solve this difficulty especially if we remember that $(\rho-1)$ for $Si^{28}F$ and $Si^{30}F$ is fairly large (−0.0136) and ν_e will be shifted by about 80 cm. $^{-1}$.

TABLE II.

Δ G′ (v), β-*Bands.*

	0−1	1−2	2−3	3−4	4−5
P− P	999·5	990·8	980·2	973·2	961·4
Q−Q	1001·6	991·1	982·6	973·1	963·7

Using the values obtained from the Q heads the following equation is derived from the weighted means for the second differences :—

$$\nu_{\text{head}} = \begin{matrix}34555\cdot7\\716\cdot6\end{matrix}\Big\} + (1006\cdot4\ v' - 4\cdot8\ v'^2) - (852\cdot0\ v'' - 4\cdot7\ v''^2).$$

The γ- *and the* δ-*Bands.*

The structure of the γ-bands is similar to that of the β-bands. Each band consists of two P and two Q heads and they appear as double-headed bands because of the overlap of successive sequences, the electronic separation, which is the same as in the β-bands, being greater than the difference between the two vibrational frequencies. Table III contains

TABLE III.

Analysis of γ-*Bands.*

v' \ v''	0	1	2	3	4	5
0	P 39341·2 (3) Q 369·1 (5) P 503·2 (5) Q 531·5 (6)	38496·6 (2) 522·8 (5) 659·7 (3) 683·8 (5)	37664·4 (1) 685·3 (3) 827·3 (2) 847·2 (3)			
1		39370·3 (7) 401·7 (3) .. 562·3 (3)	38536·5 (3) 565·0 (2) 702·8 (2) 727·1 (2)	.. *vd* 37735·9 (1) 876·3 (2) 897·1 (2)		
2			.. 39430·0 (3) .. 591·4 (1)	38574·8 (2) 602·4 (2) 740·6 (2) 764·5 (2)	37760·7 (1) *d* 781·8 (1) 926·0 (1) 945·0 (1)	
3					38609·7 (2) *c* 638·8 (2) 775·9 (2) 800·7 (2)	37798·8 (1) .. 968·2 (1) ..
4						.. 38685·6 (2) 809·8 (2) *d* 834·5 (1)

an analysis of these bands. As will be seen from the data given in Table VII later, there is little doubt, that the final state of these bands is the same as that of the β-bands. The mean vibrational differences for the initial state are :—

TABLE IV.

$\Delta G'(v)$, *γ-Bands.*

	0—1	1—2	2—3	3—4
P—P	873·8	864·3*	849·5	841·6*
Q—Q	879·3	865·8	855·9	

These data are not so numerous as in the β system and therefore the vibrational function derived is likely to be in error. For instance, the values marked with asterisks are each obtained by a single observation. Even in the Q heads already the 2–3 frequency is rather a mean of two values only, one of which is obtained from bands which are either confused or diffuse. Using the values weighted with due consideration to these facts, and taking for the final state the same function as for the β-bands, we obtain the following equation :—

$$\nu_{\text{head}} = \left.\begin{matrix} 39369\cdot1 \\ 531\cdot5 \end{matrix}\right\} + (885\cdot5\,v' - 6\cdot2\,v'^2) - (852\cdot0\,v'' - 4\cdot7\,v''^2).$$

If, however, the data on the P heads are used, $\omega'x'$ comes out to be only 5·3 and this would make a big increase in the dissociation energy. We shall deal with this later. The electronic separation, obtained as a mean from the Q heads, comes out to be 161·8 cm.$^{-1}$, as compared to 161·1 cm.$^{-1}$ the β-bands. This we take as evidence for the $^2\Sigma$ nature of the upper level though of course a $^2\Delta$ term with an insignificant electronic separation would just as well be valid.

We now come to the δ-bands which are described to be headless. The two vibrational functions of the γ-bands are close and the initial decreases more rapidly than the final so that already for the band (3, 0) and (3, 1) they will be practically identical and bands involving such transitions will be headless. The accuracy of measurement naturally cannot be very great and within such probable limits of inaccuracies it will be possible to include these headless bands in Table III. We have not included them, however, there, but the following Table V will show how the strongest of them could be classified on this basis.

TABLE V.

Classification of the Stronger δ-Bands.

ν	Intensity	Classification	
39498	3	Q_1 (4—4)	
39674	2	Q_2 (4—4)	
40261	2	Q_1 (2—1)	
40337	1	Q_1 (5—4)	
40424	4	Q_2 (2—1)	
40510	4	Q_2 (5—4)	
41100	3	Q_1 (3—1)	
41276	5	Q_2 (3—1)	
41959	4	Q_1 (3—0)	
42121	1	Q_2 (3—0)	
39341·2	3	P_1 (0—0)	Included in Table III.
39369·1	5	Q_1 (0—0)	

The α-Bands.

These bands are easily the most complicated. As shown in Table VI each band has again four heads. This apparently suggests a transition in which Λ changes by 1. This would mean the existence of Q heads which, however, are certainly not present as is clear from the partial rotational analysis given by Johnson and Jenkins. Further corroboration of this fact has been supplied recently by Badger and Blair[3] who have reported a revision of the rotational analysis. This band, which is thus analysed, is that at 22886·2 cm.$^{-1}$. It consists of two strong branches, has an unmistakable null-point at a distance of about 18 cm.$^{-1}$ from the head and therefore cannot be the head of a strong Q branch which it would be if the transition involved a change of Λ. It is certainly therefore an R head and if any Q heads were present, they would have been near about the null-point. Such heads at an average distance of about 18 to 25 cm.$^{-1}$ are present for instance in the

[3] R. M. Badger and C. M. Blair, *Phys. Rev.*, 1935, **47**, 881.

TABLE VI.

Analysis of α-Bands.

v' \ v''	0	1	2	3	4	5	6	7	8
0	*d* 23613·4 (6)	22780·0 (4)							
	573·9 (10?)	729·9 (9)							
	448·4 (6)	613·4 (6)							
	411·6 (8)	565·9 (10)							
1		23440·1 (5)	22608·1 (3)	*e* 21796·1 (2)	..				
		404·3 (8)	568·1 (9)	..	..				
		272·4 (5)	442·9 (7)	..	..				
		242·4 (7)	405·4 (8)	577·3 (3?)	20761·4 (4)				
2			23254·5 (3)	22434·3 (3)	21620·3 (3)	..			
			226·6 (7)	399·2 (7)	577·3 (3?)	20773·4 (3)			
			090·1 (7)	267·5 (7)	*d* 455·5 (2)	..			
			064·9 (8)	236·8 (9)	413·3 (2)	610·7 (6)			
3				23066·4 (2)	*c* 22252·8 (2)	..	..		
				041·8 (6)	222·9 (7)	..	..		
				22901·2 (5?)	*d* 086·4 (7)	..	..		
				886·2 (20)	*d* 061·0 (9)	21252·6 (1)	20448·4 (4)		
4					*c* ..	*d* 22061·0 (9)	..	..	
					c ..	*c* 040·2 (7)	..	*c* ..	
					22718·3 (10)	21900·1 (6)	21099·6 (2)	*a* 20315·8 (1)	
					..	*d* 878·1 (8)	..	*a* 284·1 (2)	
5					23485·1 (8)		*d* (21878·1) (8)	..	..
					451·5 (2)		851·4 (6)	..	..
					..		708·5 (3)	20910·7 (2)	..
					..		687·8 (5)	..	*a* 20111·9 (1)
6								..	
								21655·4 (4)	
								508·6 (2)	
								d 497·1 (3)	

β- and γ-bands, but are completely absent here. According to our analysis this band is a (3, 3) band and the abnormal intensity is certainly due to the fact that it is not a single band but has superimposed upon it another band, probably a (4, 4) band with about the same wavelength.

The Q heads being ruled out, the transition must be one involving no change in Λ and since the final state of these bands is identical with that of the β- and γ-bands, the transition involved is $^2\Pi \rightarrow {}^2\Pi$. The existence of four heads in such a transition is unusual but is possible if the Ω selection rule no longer holds. This happens, when one of the terms approaches more to Hund's case *b*. We believe that such a condition obtains here and that the four observed heads are due to $^SR_{21}$, R_1, R_2, and $^QR_{12}$ branches respectively. A similar case occurs in the ultra-violet bands of O_2^+, where, however, the strong $^SR_{21}$ and $^QR_{12}$ branches do not go to form heads. That they form heads in SiF is apparently due to the fact that the heads are formed at relatively high J values.

It is not obviously possible to deduce a strict value for the electronic separation of the R heads because this cannot be constant from band to band. If we take the mean separation between R_1 and R_2 heads, we obtain 132·2 cm.$^{-1}$ which gives for the upper $^2\Pi$ state an electronic separation of (161·1 − 132·2) = 28·9 cm.$^{-1}$. This incidentally shows, that the upper $^2\Pi$ state is also regular and not inverted. From the low magnitude of the electronic separations in both the upper state and particularly in the ground state, it appears as if the latter one, or, may be, both terms approach Hund's case *b*. The vibrational differences for the final state are included in the following Table VII along with those of the β- and γ-bands. From this comparison it can be concluded that the final levels of all the three systems are identical.

TABLE VII.

Comparison of $\Delta G''(v)$ *values.*

		0—1	1—2	2—3	3—4	4—5	5—6	6—7
β-Bands	P—P	845·7	835·9	826·6	816·8	809·8	(792·3)	—
	Q—Q	847·3	838·2	828·0	817·7	811·5	(800·8)	—
γ-Bands	P—P	844·1	832·8	827·1	814·4			
	Q—Q	847·0	836·5	828·7	820·1			
α-Bands	R—R	839·5	833·7	823·1	817·8	808·4	(802·4)	(790·8)

The vibrational differences of the Q heads of the β- and γ-bands agree very well indeed and those of the α-bands generally as well as can be expected from the values which are obtained as means of all the four R heads. The value 839·5 for the first vibrational difference in these bands as compared with the same difference obtained in the other bands indicates, if real, a perturbation in the first two levels of the initial state of the system.

The mean vibrational differences for the initial state are given in the following table :—

TABLE VIII.

$\Delta G'(v)$, *α-Bands.*

0—1	1—2	2—3	3—4	4—5	5—6
667·5	651·7	639·6	628·7*	601·8*	597·9*

On account of the absence of Q heads the mean differences thus obtained are not equally reliable and particularly those marked by asterisks are obtained from a few measurements only. It is quite likely therefore that the vibrational function derived from these values will be slightly in error. Due consideration to this fact will be given later when we come to discuss the dissociation products. Using for the final vibrational function that obtained from the more accurate data of the β-bands, we derive the following equation to represent the bands of the α system :—

$$\nu_{\text{head}} = \left.\begin{matrix} 23613\cdot4 \\ 573\cdot9 \\ 448\cdot4 \\ 411\cdot6 \end{matrix}\right\} + (674\cdot4v' - 6\cdot9\,v'^2) - (852\cdot0\,v'' - 4\cdot7\,v''^2).$$

Unclassified Bands.

The analysis given includes all the bands in the β and γ systems of Johnson and Jenkins except one or two, which are very weak ; most of the strong bands listed in the so-called δ system are shown also as part of the γ system and the weaker ones probably belong also to the same system. Among those listed in the α system all the strong ones are accounted for but there are a few with an intensity less than about 2 which cannot be fitted in the scheme. The bands thus unaccounted for are not only all weak but most of them are also diffuse or confused with other bands and some of them are measured approximately only. A more careful investigation would, we believe, be necessary to assign them properly either as main bands of the system or as isotopic heads.

The only system which we have not been able to analyse is the ϵ system. These bands are degraded towards the violet and very few of them are strong. We believe the data are not sufficient, but from the fact that they are degraded towards the violet, the vibrational frequency in the initial state will be bigger than that of the ground state, which, we believe, will be identical with that of the other systems. We offer further remarks about this system later.

Intensity Distribution.

The intensity distribution of all three systems is shown in Tables IX (*a* to *c*). In the β-bands the intensity distribution is roughly analogous to that shown in Fig. 16 (*a*) in Jevons' *Report*[4] with a pronounced bias towards the initial level. This is in conformity with the greater energy of dissociation which the molecule has in the initial state. The α-bands, on the other hand, correspond to a distribution given in Fig. 16 (*c*) of Jevons' *Report* with a pronounced stability of the lower state. The γ-bands show an intensity distribution of the type given in Fig. 16 (*b*) of the above *Report*. On account of the near equality of the ω values, the bands are confined to a few long sequences, not involving big changes of v. This indicates that our interpretation of the headless bands is very probably correct. We believe also that the energy of dissociation of the upper state is more likely to be equal to or slightly bigger than that of the lower state, and not smaller than

TABLE IX.

Intensity Distribution.

(*a*) β-*Bands.*

v' \ v''	0	1	2	3	4	5	6
0	8	10	5	2	0		
1	8	2	8	5	2	0	
2	3	5		4	3	2	0
3		3	3	1*vd*	1	1	2*vc*
4			2	0	2*vd*		
5				2		1*vd*	
6					0		

[4] W. Jevons, *Report on Band Spectra*, London, 1932, p. 69.

TABLE IX. (*b*) *γ-Bands.*

v' \ v''	0	1	2	3	4	5
0	5	4	2			
1		4	2	2		
2			2	2	1	
3					2	1
4						2

TABLE IX. (*c*) *α-Bands.*

v' \ v''	0	1	2	3	4	5	6	7	8
0	8	8							
1		6	7	2	4				
2			6	7	3	5			
3				6	6	1	4		
4					8	8	2	2	
5					4		6	2	1
6								3	

it, as obtained from extrapolation of the above vibrational function. The correlation of the products of dissociation of the upper state to atomic terms also points in this direction, as will be seen later.

Dissociation Energy and Electronic Configuration.

The energies of excitation and dissociation of the observed terms of the molecule are given in volts together with the excitation energies of the dissociation products in the following Table X and in the diagram of Fig. 1.

TABLE X.

Dissociation and Excitation Energy.

Term	ν_0 (volts)	D (volts)	$\nu_0 + D' - D''$
$X\,^2\Pi$	0	4·77	0
$A\,^2\Pi$	2·91	2·04	0·18
$B\,^2\Sigma$	4·28	6·51	6·03
$C\,^2\Sigma$	4·88	3·90	4·01

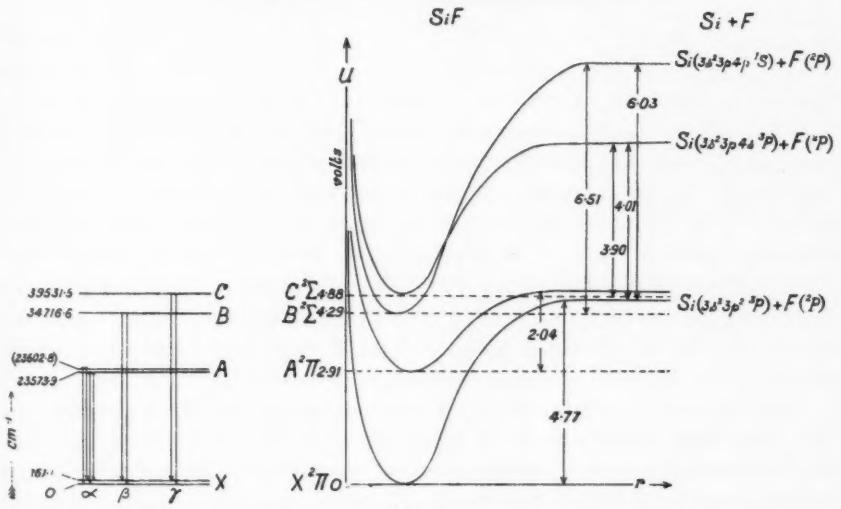

FIG. 1.

We now proceed to discuss the correlation of the molecular levels to those of the separated atoms and thus select the most probable electronic configurations of the molecule in its four states from the various possible ones. The ground state $X\,^2\Pi$ of the molecule arises from unexcited atoms Si $(3s^2\ 3p^2,\ ^3P)$ + F $(2s^2\ 2p^5,\ ^2P)$.

From these configurations we derive the following structure:

$$\ldots\ldots\sigma^2(s)\ \sigma^{*2}(s)\ \pi^4(p)\ \sigma^2(p)\ \pi^*(p)\ldots\ldots\ldots X\,^2\Pi.$$

The level $A\,^2\Pi$ involves the same unexcited atoms; the difference of 0·18 volts between the dissociation products is well within the errors of extrapolation or, if real, might be attributed to the electronic separation

of one or both of the constituent atoms. It must, however, be remembered that the constants for this level are derived from the R heads and the vibrational frequency differences obtained are fewer as well as less satisfactory than those of the B $^2\Sigma$ and X $^2\Pi$ levels of the molecule. Still, there appears to be little doubt, that the curve runs to the same convergence limit as that of the ground-level. These considerations show that the electronic configuration of this state does not involve a change in the principal quantum number of the electrons. Furthermore, it cannot be the $\pi^*(p)$ electron, which without change in the principal quantum number can be transferred to the $\sigma^*(p)$ group only, because the resulting molecular term would then be $^2\Sigma$. Therefore we have only to consider the excitation of one of the inner p-electrons. The following are the three possibilities in this case :—

$$\ldots\ldots\pi^4(p)\ \sigma(p)\ \pi^{*2}(p) \quad .. \quad .. \quad .. \quad .. \quad (1)$$

$$\ldots\ldots\pi^4(p)\ \sigma(p)\ \pi^*(p)\ \sigma^*(p) \quad .. \quad .. \quad .. \quad (2)$$

$$\ldots\ldots\pi^3(p)\ \sigma^2(p)\ \pi^{*2}(p) \quad .. \quad .. \quad .. \quad .. \quad (3)$$

The first of these is to be ruled out because it does not give rise to a $^2\Pi$ level. It is difficult to choose between the possibilities (2) and (3) which are both probable. Since the energy of dissociation in this state is considerably less than in the ground state without an increase of the principal quantum number of the electrons, it is one of the bonding electrons, that is excited. From the point of view of the electron pair bond theory of linkage, the electron from one of the groups $\sigma^2(p)$ or $\pi^4(p)$ whichever contains a p-electron contributed by the Si atom, will be bonding, the second p-electron of Si being the odd electron in the group $\pi^*(p)$. From the other view-point both groups are non-premoted and therefore bonding.

The level B $^2\Sigma$ is interesting. The constants for this level are particularly more reliable than those for A $^2\Pi$ and C $^2\Sigma$. We expect therefore that the extrapolated energy of dissociation, which is derived from the constants deduced from the Q heads is accurate. It clearly indicates a strong increase in bond energy. From analogy with many other molecules, in which a similar situation obtains we ascribe this increase to the excitation of the odd $\pi^*(p)$ electron, which has been shown in numerous cases to have nothing to do with the linkage but to disturb it. Indeed the energy of 6·03 volts between the dissociation products of this and the normal state is in complete accord with 6·16 volts which is the difference

$$2s^2\ 3p^2,\ ^3\mathrm{P} - 3s^2\ 3p\ 4p,\ ^1\mathrm{S},$$

of Si. Accordingly the $\pi^*(p)$ odd electron is taken to one of the $\sigma(p)$ groups of the next principal quantum number, probably the non-premoted one. We therefore assign the following configuration to this level :—

$$\ldots\pi^4(p)\ \sigma^2(p)\ldots\ldots\sigma(p) \qquad \mathrm{B}\ ^2\Sigma.$$

This therefore furnishes another example in favour of the pair-bond view. Extending this view we should expect some other terms with increased energy of dissociation arising from configurations of the atom Si such as $3p$ 4s, ^{3}P which also would give structures of the molecule in which the odd electron is excited. Such a molecular term originates at 4·9 volts (the energy of excitation of ^{3}P) and if we assume a dissociation energy similar to that of B $^2\Sigma$, we obtain for the excitation of the molecule about 3 volts. It is not unlikely that the bands of the so-called ϵ system with 23898 cm^{-1} as one of its strongest bands belong to such a state. These bands are degraded towards the shorter waves, as we would expect them to be on account of increased energy of dissociation.

The $\Delta G'(v)$ values for the C $^2\Sigma$ level are not so numerous and therefore not so satisfactory as those of the β-bands. They should, however, be more reliable than those for the A $^2\Pi$ level because here we can deduce them from the Q heads. We remark here simply that the data on P heads yield for $\omega'x'$ 5·3 while those on Q heads give 6·2. The dissociation energy is extrapolated from the latter values and it appears as if it is slightly too low. As a matter of fact, there is no term in Si and of course none in F which can be correlated to 4·01 volts which is the excitation of the products of dissociation of this level. We therefore attribute this level to

$$F\ (^2P) + Si\ (3s^2\ 3p\ 4s, {}^3P),$$

which gives an excitation energy of 4·90 volts. Indeed, if we would use for $\omega'x'$ the value 5·3 obtained from data on P heads, we get a dissociation energy of 4·6 volts and an excitation energy of 4·7 volts for the products of dissociation. On this basis the electronic configuration would contain a $\sigma(s)$ electron of the next higher main quantum number which has been a p-electron in the X $^2\Pi$ level. It cannot be an electron from the $\sigma^2(p)$ group because the resulting configuration $\sigma\pi\sigma$ cannot give a $^2\Sigma$ level. Therefore it must be one of the premoted or non-premoted π-electrons. By assuming an excitation energy of 4·90 volts for the dissociation products the energy of dissociation of the C $^2\Sigma$ level becomes 4·81 volts. This value is almost identical if not higher than that for the ground-level. This is not improbable in view of the fact that the γ-bands are shaded towards the shorter wave side, which certainly means a decrease in the internuclear distance and probably, but not always, an increase of the bond energy. In view of this, we rather believe that it is the $\pi^*(p)$ electron, which is excited to the next higher $\sigma(s)$ group and the electronic configuration would then be the following :—

$$\ldots.\pi^4(p)\ \sigma^2(p)\ldots.\sigma(s) \qquad C\ ^2\Sigma.$$

The theoretical implications will be discussed at greater length in a forthcoming paper.

THE DESIGN OF FALLS WITH REFERENCE TO UPLIFT PRESSURE.

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Received March 4, 1936.

Introduction.

In a series of investigations,[1, 2] carried out in the Institute, it was definitely established that the distribution of uplift pressure under hydraulic works such as weirs and dams follows the same law as the distribution of electrical potential in conductors. Having established this fact, the method is now employed for the investigation of uplift pressure under hydraulic works. The details of the method are described in the papers referred to above. Since then a number of standard cases,[3, 4] and actual weirs[5] have been investigated by this method.

In the present paper, it is proposed to give an account of the investigation of the uplift pressure under hydraulic works on porous foundations, such as are built in canals and rivers.

Construction of Falls.

Fig. 1 represents the cross-section of a fall with a length L_1 for the upstream apron, L_2 for the downstream apron, depth d_1 for the fall and d_2

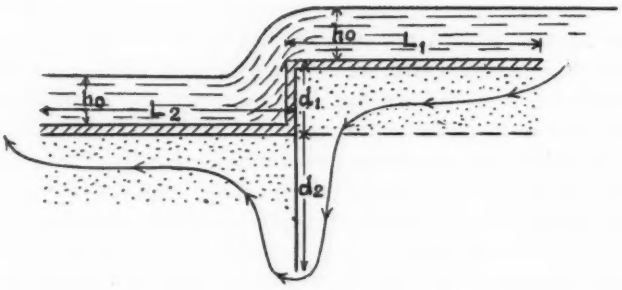


Fig. 1.

for the sheet pile. There is a depth h_0 of water upstream and a similar depth of water downstream. As illustrated in the figure, there is a difference of head equal to d_1 and due to the seepage flow taking place through the porous subsoil, this head exerts an uplift pressure on the masonry. If there is a lock and there is only water on the upstream side then the head d_1 increases to $d_1 + h_0$, since there is no water downstream. It is necessary to know the residual pressures at any point and its distribution for purposes of design.

Results.

Two series of experiments were carried out. In the first series, the lengths of downstream apron were varied, the fall d_1 and the length of the sheet pile d_2 being kept constant. The length, L_1 of the upstream apron in the model was maintained at four inches, the fall d_1 one inch and the length of the sheet pile d_2 4″ throughout this series. In the second series, the lengths of the downstream and upstream aprons and the depth of the fall were kept constant and the length of the sheet pile varied from 0 to 5″. Nine cases of the former series and eight cases of the latter series were investigated and complete pressure contours were plotted. Fig. 2 shows one such case as an illustration. The pressure contours of the remaining sixteen cases

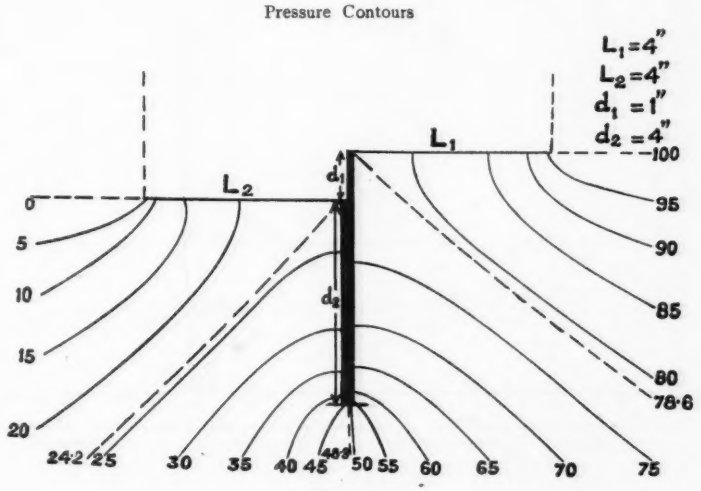


FIG. 2.

are not shown here as the types are similar. From the engineering point of view, the hydraulic gradient along the underside of the masonry is the most

important consideration, since it is this gradient that measures the uplift pressure at any point.

Fig. 3 shows the pressure distribution under the masonry for different values of I_{r2}. The drop in pressure caused by the sheet pile is shown by the discontinuities in the curves. The percentage drop in pressure is marked for each graph.

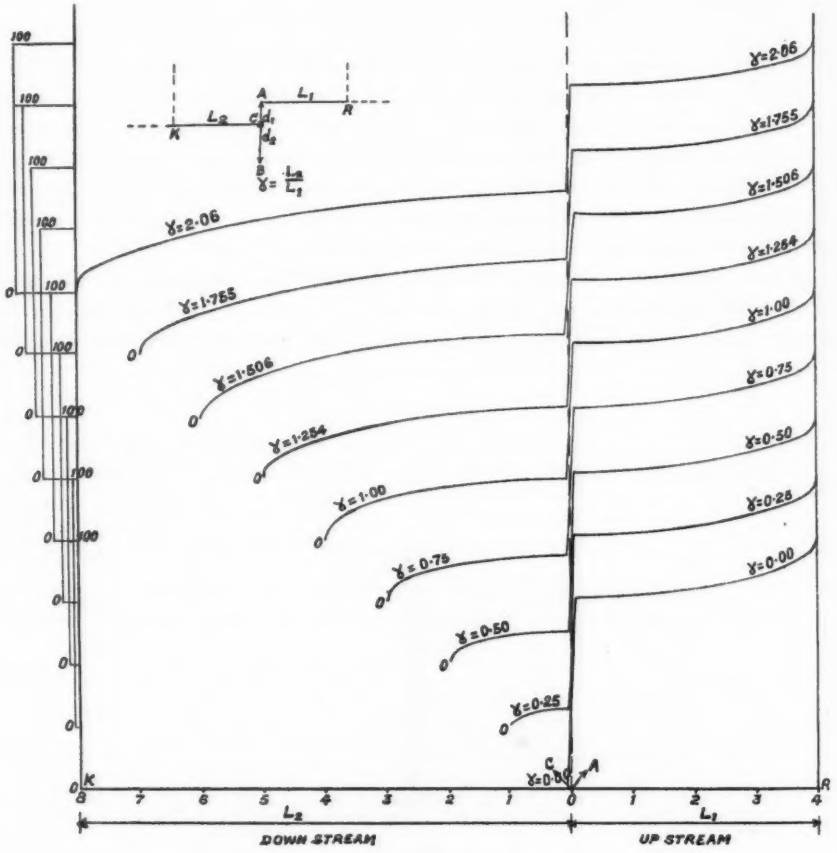


FIG. 3.

While the total drop of pressure caused by the sheet pile is shown by the discontinuity of lines in Fig. 3, the actual distribution along the sheet pile is shown in Fig. 4. It may be seen from this figure that while L_2

changes from 0 to 8″ in the model, the changes of pressure at the upstream sides of the sheet piles are not very considerable. This point is of importance in connection with the application of the results to design.

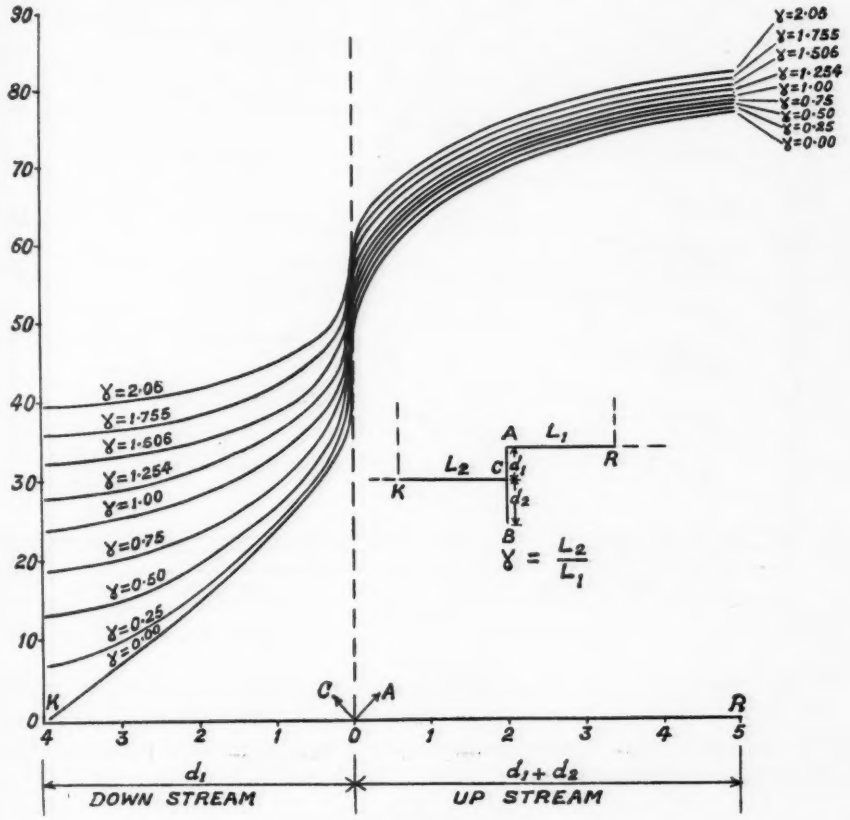


FIG. 4.

Fig. 5 shows the distribution of pressure when the lengths d_2 of the sheet pile change from 0 to 5″. L_1 and L_2 were maintained at 7″ in all the experiments referred to in this figure. Again while the total drop of pressure along the sheet pile is given by the discontinuity in the curves in Fig. 5, the nature of the distribution of pressure along the sheet pile is given by Fig. 6. As is seen in Fig. 6, the dotted line joining the pressures

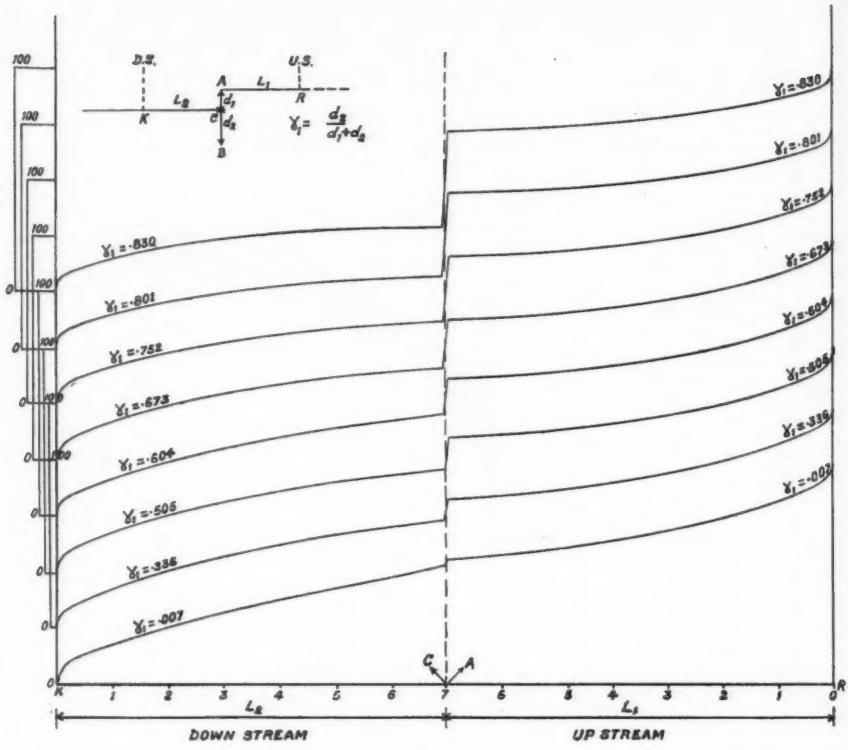


FIG. 5.

at the corners A and C (*i.e.*) the ends of the pressure distribution curves, has only a very small curvature. The value of the pressures at A and C for any particular combinations of $d_2/d_1 + d_2$ can thus be obtained from this curve, by interpolation.

On the Design of Falls.

When a fall is to be designed for a particular combination of floor and sheet pile, the best method is to subject the design to an experimental examination. In the Punjab, this is always done.

The results of the present investigation can be used for the ordinary combinations of sheet pile and floor, but it is not possible to apply the results so far obtained to all possible designs. There is no accurate theoretical expression by means of which the uplift pressure can be derived for every such case of a fall. Comparison of the present data shows that

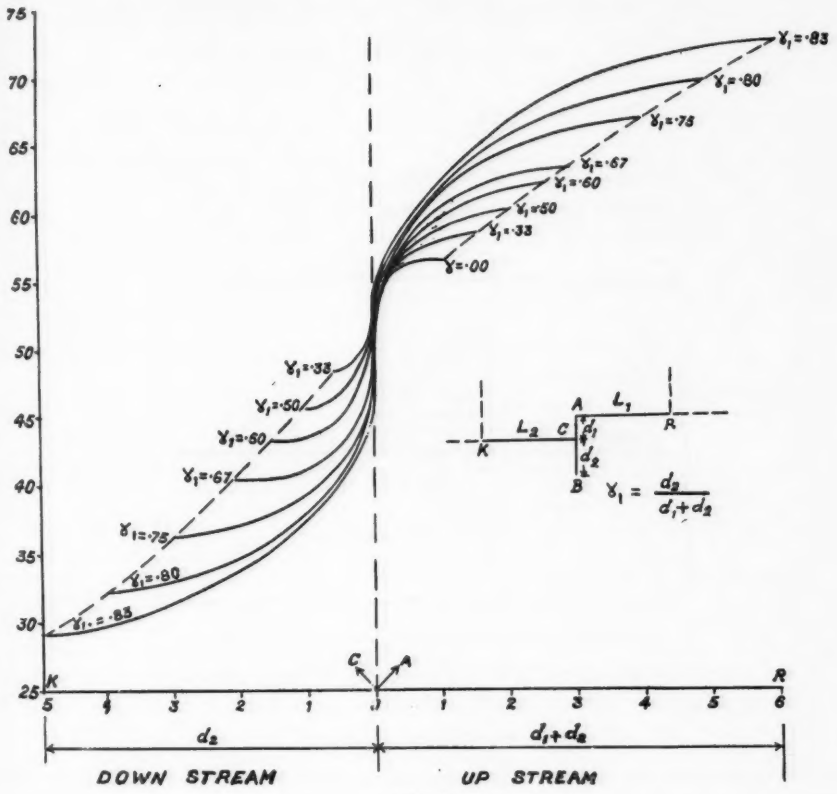


FIG. 6.

the pressure distribution for the type of works indicated by the model in Fig. 1, corresponds very nearly with those of a single sheet pile case under a flush floor, when the fall d_1 is small compared with L_1 and L_2 and sheet-pile not at the heel or toe. For such a case, namely, a sheet pile under a simple floor, as is shown in Fig. 7, a complete theory has been worked out by Weaver.[6] The expression to find the pressure on the base of the dam is, according to him,

$$p\,(x, y) = \frac{p_0}{\pi}\, c\,(x, y) = \frac{p_0}{\pi} \cos^{-1}\left[\frac{d\,(\chi - \lambda) \pm \sqrt{x^2 + d^2}}{d\,\lambda}\right]$$

the origin $x = 0$ corresponding to the position of the pile and the value of x increasing from the upstream to the downstream side. In this expression

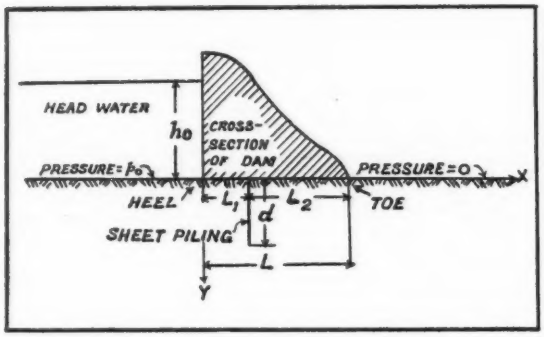
$$\chi = \sqrt{1+\alpha_1^2}$$

$$\lambda = \frac{\sqrt{1+\alpha_1^2} + \sqrt{1+(\alpha-\alpha_1)^2}}{2}$$

$$\alpha_1 = \frac{L_1}{d} \quad \text{and} \quad \alpha = \frac{L}{d}$$

d = depth of the sheet pile and

L = length of the floor. (See Fig. 7.)



Reproduced from the *Journal of Mathematics and Physics*, June 1932 (W. Weaver).

FIG. 7.

If it is desired to obtain an approximate value of the uplift pressure without recourse to an experiment, in the absence of a general solution Weaver's expression may be applied to the case of falls as has already been stated. In applying this equation to the case of a fall, $d_1 + d_2$ may be regarded as the length d of the pile for purposes of calculation on the upstream side and d_2 for the length of the pile on the downstream side. The justification for so doing lies in the fact that, as seen from Fig. 4, the changes in L_2 between limits shown in the figure do not affect the nature of the distribution of pressure on the upstream side by any appreciable amount.

Adopting such a method of calculation as is indicated here, the results of a comparison between the theory and experiment are shown in the table. The extreme variation is about 8%. It is generally much less as can be seen by comparing columns 3 and 4, and 7 and 8 in the table. This degree of accuracy is sufficient for practical purposes, since a factor of safety is usually introduced in the design.

Comparison between the Theoretical and Experimental Values.

(For Positions of A and C, see Inset in Fig. 3.)

UPSTREAM SIDE P_A denotes pressure at A				DOWNSTREAM SIDE P_C denotes pressure at C				
a	a_1	P_A Theoretical	P_A Experimental	a	a_1	P_C Theoretical	P_C Experimental	
0·800	0·80	77·2	77·0	1·00	1·00	0·0	0·0	
1·000	0·80	77·3	77·1	1·25	1·00	7·3	6·8	
1·200	0·80	77·6	77·4	1·50	1·00	13·8	12·9	
1·400	0·80	78·0	78·2	1·75	1·00	19·8	18·7	L_2 varying;
1·600	0·80	78·5	78·6	2·00	1·00	25·0	24·2	L_1, d_1 and d_2
1·800	0·80	79·1	79·3	2·25	1·00	29·5	27·9	constant.
2·000	0·80	79·7	79·9	2·50	1·00	33·3	31·9	
2·200	0·80	80·2	80·7	2·75	1·00	36·6	37·1	
2·400	0·80	80·7	81·7	3·00	1·00	39·5	39·4	
9·33	4·67	56·7	58·4	28·00	14·00	47·7	48·2	
7·00	3·50	58·8	60·2	14·00	7·00	45·5	45·6	
5·60	2·80	60·9	62·1	9·33	4·67	43·3	43·3	d_2 varying;
4·67	2·33	62·9	63·2	7·00	3·50	41·1	40·4	L_1, L_2 and d_1
3·50	1·75	66·5	66·9	4·67	2·33	37·1	36·2	constant.
2·80	1·40	69·7	69·7	3·50	1·75	33·5	32·3	
2·33	1·17	72·6	72·6	2·80	1·40	30·2	29·2	

Other Considerations.

One important point in the design of such works is the pressure gradient at the toe. When the water escapes from beneath the work in an upward direction, the incoherent material from below the masonry is removed by the water. This causes cavities to form under the works and frequently such a work will fail at the toe. If a sheet pile is driven at the toe, this pressure gradient flattens as can be shown both experimentally and theoretically. The toe has, therefore, to be protected by a suitable length of piling or depressed masonry. The correct length of this piling or depression has to be estimated taking various considerations such as stratification head, etc. into account. When once the length of this piling is fixed, there is a specific length for the floor, which will give the maximum safety. Any extra length does not add to the safety as might be expected.

An important factor is the geological stratification with its consequent modification of the pressure distribution. When stratification is known to occur, the pressure distribution can only be determined by an experiment

in which the stratification is reproduced. The effect of stratification will be appreciable only if it occurs near the work. As has been pointed out by Weaver, " the distortion which a sheet piling produces in the lines of flow does not extend as far from the piling as one might expect. The distortion due to the piling extends a distance in all directions equal, roughly to the piling depth. The interest in this observation lies in the strong suggestion that non-homogeneities in the foundation material very likely are effective in disturbing seepage flow only in a neighbourhood, whose dimensions are roughly twice those of the non-homogeneity. One has thus a crude means of judging, when and to what extent is applicable an analysis based on homogeneity."

Summary.

In this investigation the uplift pressures under hydraulic works on porous foundations, such as are built at the falls in canals and rivers, have been determined.

Two series of experiments have been carried out and the pressure distributions have been obtained for ordinary combinations of sheet pile and floor. A method of obtaining the pressure distribution approximately by the application of theory has also been indicated.

Our thanks are due to Dr. E. McKenzie Taylor, the Director, for his keen interest in the problem.

REFERENCES.

1. Gurdas Ram, V. I. Vaidhianathan and E. McKenzie Taylor, *Proceedings of the Indian Academy of Sciences,* 1935, **2**, 22.
2. V. I. Vaidhianathan and Gurdas Ram, *Research Publication* of the Irrigation Research Institute, Punjab, Lahore, 1935, **5**, 4.
3. V. I. Vaidhianathan, Gurdas Ram and E. McKenzie Taylor, *Proceedings of the Indian Academy of Sciences,* 1935, **2**, 646.
4. V. I. Vaidhianathan, Gurdas Ram and E. McKenzie Taylor, *Research Publication* of the Irrigation Research Institute, Punjab, Lahore, 1936, **5**, 6.
5. V. I. Vaidhianathan and Gurdas Ram, *Punjab Engineering Congress,* 1936, No. 190.
6. W. Weaver, *Journal of Mathematics and Physics,* 1932, **11**, 114.

STUDIES ON THE ANISOTROPY OF THE OPTICAL POLARISATION FIELD IN LIQUIDS—PART III.

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1. *Introduction.*

In Parts I and II of this series (Sundara Rama Rao, 1936) the dependence on the temperature of the molar refractivities and the anisotropic coefficients of the optical polarisation field in some typical non-associating liquids has been studied. A brief discussion was given on the significance of the results to the subject of light-scattering. In this part, it is proposed to extend the above investigations to some typical associated liquids. The results already available in the case of water are examined and three other liquids, namely, nitrobenzene, acetic acid and formic acid are studied here for the first time.

2. *Experimental.*

In this investigation, a Pulfrich refractometer has been used for the measurement of refractive indices. This instrument has a double advantage over the Abbe refractometer in that it yields greater accuracy in measurement and can be used for such corrosive liquids as formic and acetic acids.

The refractometer having been tested for zero error, the prism is connected to a copper heater supplied with a steady flow of water from a constant pressure head. Two accurate thermometers reading to $0{\cdot}1°$ over the ranges $0–50°$ and $50°-80°$ are provided with the instrument together with a correction chart for the readings. Measurements of refractive indices are made with an electric sodium vapour lamp and all the values therefore refer to λ 5893 A.U.

3. *Results.*

The refractive indices and the densities at different temperatures which are already available in the case of water* are given in Table I. The molar refractivities calculated from these data are shown in the last row of this table. Tables II, III and IV contain the refractive indices obtained in the present investigation at different temperatures for formic acid, acetic acid and nitrobenzene respectively. The densities given in these tables are also taken from *I. C. T.* and the molar refractivities are calculated therefrom at all the temperatures at which the refractive indices have been measured.

* *Landolt-Bornstein Tabellen* and *I. C. T.*, Vol. III.

TABLE I.

Molar Refractivity of Water.

Temp.	0	10	20	30	40	50	60	70	80
Ref. Index ..	1·33381	1·33360	1·33330	1·33202	1·33069	1·32908	1·32718	1·32516	1·32300
Density ..	0·99987	0·99973	0·99823	0·99568	0·99225	0·98807	0·98324	0·97781	0·97183
Mol. Refractivity ..	3·71447	3·71288	3·71238	3·71196	3·71122	3·71043	3·70907	3·70871	3·70894

TABLE II.

Molar Refractivity of Formic Acid.

Temp.	30	35	40	45	50	55	60	65	70
Ref. Index ..	1·36725	1·36543	1·36343	1·36146	1·35958	1·35798	1·35585	1·35365	1·35140
Density ..	1·20873	1·20259	1·19644	1·19028	1·18409	1·17789	1·17167	1·16541	1·15913
Mol. Refractivity ..	8·55426	8·55975	8·56152	8·56396	8·56851	8·57916	8·57855	8·57662	8·57365

TABLE III.

Molar Refractivity of Acetic Acid.

Temp.	30	35	40	45	50	55	60	65	70	75
Ref. Index ..	1·36963	1·36816	1·36680	1·36525	1·36343	1·36137	1·35958	1·35753	1·35532	1·35304
Density ..	1·0388	1·0335	1·0282	1·0229	1·0175	1·0120	1·0065	1·0009	0·9952	0·9895
Mol. Refractivity ..	13·0591	13·0793	13·1033	13·1212	13·1320	13·1361	13·1492	13·1550	13·1567	13·1560

TABLE IV.

Molar Refractivity of Nitrobenzene.

Temp.	10	15	20	25	30	35	40	45	50	55	60	65
Ref. Index	1·55700	1·55450	1·55242	1·54947	1·54720	1·54487	1·54173	1·54018	1·53796	1·53580	1·53361	1·53123
Density ..	1·21312	1·20817	1·20322	1·19826	1·19329	1·18833	1·18335	1·17837	1·17339	1·16840	1·16341	1·15841
Mol. Refractivity	32·6610	32·6732	32·7058	32·6959	32·7196	32·7400	32·7203	32·7803	32·8068	32·8366	32·8650	32·8839

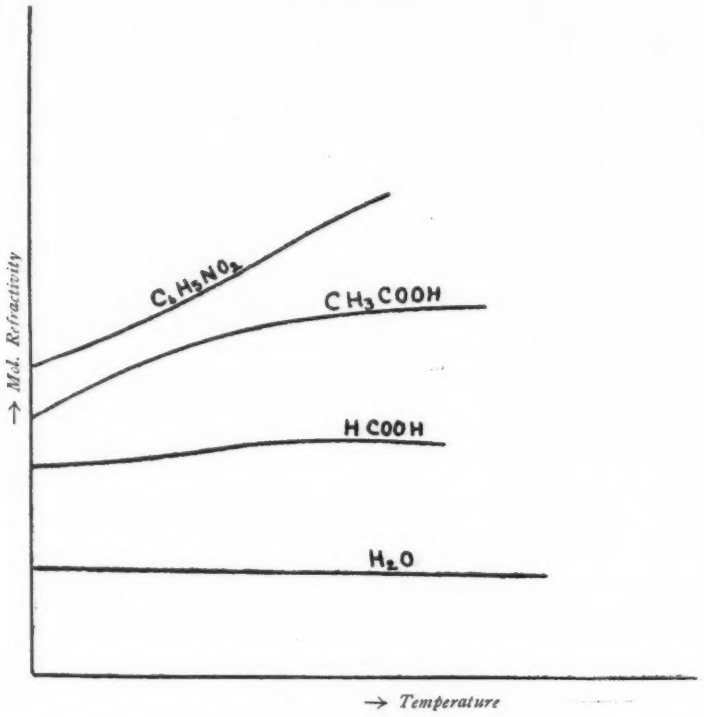

FIG. 1.

4. Some Remarks.

The curves drawn in Fig. 1 represent graphically the variation in the molar refractivity with temperature and hence the extent to which the Lorentz law breaks down in these cases. The group of liquids studied in this part are of a different type and hence behave in a manner which is slightly different from that of the liquids studied in Part I. The molar refractivity of acetic and formic acids *increases slowly up to a certain temperature and then begins to diminish.* The behaviour of nitrobenzene is similar to that of benzene. It is interesting to note that the changes in the molar refractivity of water are of a much smaller order of magnitude than those exhibited by other liquids. The curve shows that it may be regarded as practically constant in the range 0–80° C. It must however be remarked that a close examination of the results given in Table I reveals a slight but definite and progressive *diminution* in the molar refractivity of this substance as well.

5. Significance of the Results to the subject of Light Scattering.

As indicated in Part II, the results are intimately connected with the depolarisation of scattered light exhibited by these liquids at different temperatures. As the group now under investigation consists of associating molecules, it will be of interest to examine this aspect of the question also.

With the exception of water, the refractive indices of the corresponding vapours are not available for the liquids studied in this paper. Hence the method of calculation of the coefficients of the anisotropic polarisation field becomes slightly altered. If A′, C′ and C′* represent the effective principal optic moments for a liquid molecule at a particular temperature and p_1, p_2 and p_2 the corresponding coefficients of anisotropy of the polarisation field surrounding the molecule in the liquid state, the following relationships hold:—

$$\frac{n_l^2 - 1}{4\pi\nu_l} = \frac{A' + 2C'}{3} \quad .. \quad (1) \qquad \frac{r_l}{6 - 7r_l} = \frac{\nu_l (A' - C')^2}{45\, kT\beta\left(\frac{n_l^2 - 1}{4\pi}\right)^2} \quad .. \quad (2)$$

and

$$\left.\begin{aligned} \frac{4\pi + p_1 (n_l^2 - 1)}{4\pi + p_2 (n_l^2 - 1)} &= \frac{1 + 2\sqrt{\delta_l}}{1 - \sqrt{\delta_l}} \times \frac{1 - \sqrt{\delta_v}}{1 + 2\sqrt{\delta_v}} \text{ if } A > C \\ \frac{4\pi + p_1 (n_l^2 - 1)}{4\pi + p_2 (n_l^2 - 1)} &= \frac{1 - 2\sqrt{\delta_l}}{1 + \sqrt{\delta_l}} \times \frac{1 + \sqrt{\delta_v}}{1 - 2\sqrt{\delta_v}} \text{ if } A < C \end{aligned}\right\} \quad .. \quad (3)$$

$$p_1 + 2p_2 = 4\pi \quad .. \quad .. \quad .. \quad .. \quad (4)$$

$$A' = A\left(1 + p_1 \frac{n_l^2 - 1}{4\pi}\right) \quad .. \quad (5) \qquad C' = C\left(1 + p_2 \frac{n_l^2 - 1}{4\pi}\right) \quad (6)$$

n_l, ν_l and r_l represent respectively the refractive index, number of molecules per c.c. and the depolarisation of the transversely scattered light in the liquid state. A knowledge of these quantities together with that of the compressibility of the liquid at a particular temperature enables us to calculate A′ and C′ at that temperature for the various molecules from equations (1) and (2). After substituting the observed values for δ_l and δ_v the coefficients p_1 and p_2 are calculated from equations (3) and (4). Making use of the relationships (5) and (6) the values of A and C, the principal optic moments of the molecule in the vapour state are deduced from those of A′, C′ and p_1, p_2. The values of p_1 and p_2 at every temperature are thereafter calculated by the method indicated in Part II of this series with the help of equations (3) and (4) of that part. The coefficients of the anisotropic polarisation field so derived are made use of in calculating the depolarisation of

* This assumption is strictly valid only for axially symmetric molecules and can be regarded as merely an approximation in these cases.

TABLE V.
Acetic Acid.

$\delta_v \times 10^3 = 25{\cdot}9$; $\delta_l \times 10^3 = 34{\cdot}3$ $\quad$ $A = 6{\cdot}8461 \times 10^{-24}$; $C = 4{\cdot}2371 \times 10^{-24}$

Temp.	30	35	40	45	50	55	60	65	70	75
n_l ..	1·36963	1·36816	1·36680	1·36525	1·36343	1·36137	1·35958	1·35753	1·35532	1·35304
ρ_1 ..	4·994	5·167	5·374	5·531	5·627	5·669	5·788	5·845	5·872	5·876
ρ_2 ..	3·786	3·700	3·596	3·518	3·470	3·449	3·389	3·361	3·347	3·345
ρ_1/ρ_2 ..	1·319	1·396	1·494	1·572	1·622	1·644	1·708	1·739	1·754	1·757
$\beta \times 10^{12}$	..	..	104	..	..	..	..	..	..	132·5
$100r_l$ calc.	..	..	48·0	..	..	..	..	..	..	44·0
$100r_l$ obs.	..	..	42·8	..	..	..	..	..	..	34·3

TABLE VI.
Nitrobenzene.

$\delta_v \times 10^3 = 54{\cdot}7$; $\delta_l \times 10^3 = 32{\cdot}5$ $\quad$ $A = 7{\cdot}1187 \times 10^{-24}$; $C = 16{\cdot}5078 \times 10^{-24}$

Temp.	10	15	20	25	30	35	40	45	50	55	60	65
n_l ..	1·55700	1·55450	1·55242	1·54947	1·54720	1·54487	1·54173	1·54018	1·53796	1·53580	1·53361	1·53123
ρ_1 ..	6·315	6·303	6·256	6·281	6·249	6·222	6·265	6·169	6·132	6·088	6·046	6·021
ρ_2 ..	3·126	3·132	3·155	3·143	3·159	3·172	3·151	3·199	3·218	3·239	3·260	3·276
ρ_1/ρ_2 ..	2·020	2·013	1·983	1·998	1·978	1·962	1·988	1·928	1·906	1·880	1·855	1·838
$\beta \times 10^{12}$	47	..	..	..	..	..	..	..	55	..	..	..
$100r_l$ calc.	68·8	..	..	..	..	..	..	..	65·8	..	..	..
$100r_l$ obs.	..	..	..	..	..	..	..	..	66·0	..	..	..

the transversely scattered light in the liquid state by the formula already given in Part II. The results so calculated at certain temperatures are compared with the experimental values available from the work of Ramachandra Rao (1927) and Krishnan (1936) in Tables V and VI. As the necessary data are not available for formic acid, it has not been dealt with here

6. *Discussion of Results.*

It is seen from the tables that in the case of acetic acid, the anisotropy of the polarisation field increases with increasing temperature in the entire range studied. This behaviour is quite peculiar and is presumably attributable to the presence of large molecular aggregates, which break up with rise of temperature. Their presence in acetic and formic acids has an independent confirmation from the recent work of R. S. Krishnan (1936).

We will now interpret the results regarding the variation of molecular refractivity on the basis of the Lorentz law as modified by Raman and Krishnan (1928).

$$\frac{n_l^2 - 1}{n_l^2 + 2} = \frac{4\pi}{3} \nu_l \frac{A+B+C}{3}\left(1 + \nu_l \frac{A\sigma_1 + B\sigma_2 + C\sigma_3}{3}\right)$$

which transforms into

$$\frac{n_l^2 - 1}{n_l^2 + 2} \cdot \frac{M}{\rho} = \frac{4\pi}{3} \cdot N \frac{A + 2C}{3}\left(1 + \nu_l \frac{A\sigma_1 + 2C\sigma_2}{3}\right)$$

where $\sigma_1 = p_1 - \frac{4\pi}{3}$ etc. The factor responsible for the variation in the molar refractivity is $\nu_l (A\sigma_1 + 2C\sigma_2)$. Ordinarily, this factor may easily be shown to be negative and its numerical value tends to diminish with increasing temperature. As such the molar refractivity normally increases with increasing temperature, examples being C_6H_6, C_6H_{14}, etc., studied in Part I. In the case of acetic acid however $\sigma_1 > \sigma_2$ and since $\sigma_1 + 2\sigma_2 = 0$ we can write the variable factor as $\nu_l \sigma_1 (A - C)$ which is easily seen to be *positive*. Further, as the temperature rises σ_1 *increases*. Both these features are exceptional and may, to some extent, be regarded as consequences of the fact that the observed value of δ_v for acetic acid is less than the observed value of δ_l. Apart from the uncertainty involved in applying the equations to such a case, a further complication arises on account of the presence of large groups which may break up with rise in temperature. The observed curve in acetic and formic acids must be regarded as the resultant of all these factors and it is not surprising that at a certain temperature the molar refractivity ceases to increase and begins to diminish.

7. *Summary.*

The molar refractivity is found to increase with temperature in nitrobenzene and diminish, although only slightly, in the case of water. In the cases of acetic and formic acids, it increases up to a certain temperature and then begins to diminish. The coefficients of anisotropy of the optical polarisation field are calculated in the cases of acetic acid and nitrobenzene. In the former, the polarisation field becomes more and more anisotropic whereas in the latter it becomes more and more isotropic with increasing temperature.

The author is highly thankful to Mr. S. Bhagavantam for his helpful guidance in the work.

REFERENCES.

R. S. Krishnan, *Proc. Ind. Acad. Sci.*, 1936, **3**, 126.
S. Ramachandra Rao, *Ind. Jour. Phys.*, 1927, **3**, 1.
C. V. Raman and K. S. Krishnan, *Proc. Roy. Soc.*, 1928, **117**, 589.
B. Sundara Rama Rao, *Proc. Ind. Acad. Sci.*, 1936, **3**, See Parts I & II of this series.

VARIATION OF INTENSITY OF SCATTERED LIGHT WITH TEMPERATURE.

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1. Introduction.

It has been noticed in this laboratory by Veerabhadrarao* that the intensity of the Rayleigh scattering in certain liquids such as formic acid behaves in an unexpected manner in as much as it diminishes with increasing temperature. This observation, though of a qualitative nature, was quite definite and is contrary to what may be expected and to what has been observed in normal cases such as benzene.

The aim of the present investigation is to experimentally determine the intensity of the transversely scattered light at different temperatures in some typical liquids. The experimental results are compared with the values calculated on the basis of the formula given by Raman and Krishnan (1928) and an attempt has been made to explain the different behaviours exhibited by different types of liquids.

A similar investigation was undertaken earlier by Ramachandrarao (1927). He experimented upon a number of organic liquids including the fatty acids. The method of measurement was, however, based on a visual examination of the scattered light. Recently, Krishnan (1936) also carried out certain experiments wherein he had obtained the intensity of scattering at different temperatures using a photo-electric cell. In the present investigation a spectrograph has been used, thus separating the Rayleigh scattering from the Raman lines, and the method of obtaining a scale of intensity marks by varying the slit widths has been used in computing the relative intensities of the scattered light at different temperatures.

2. Experimental.

The liquid under investigation is contained in an ordinary Wood's tube with slight modification and of internal diameter $1\frac{1}{2}$ inches. The scattered light is observed through a small window in one of its ends with

* Thesis submitted to the Andhra University, 1935.

suitable arrangements to eliminate all parasitic light. The liquid is illuminated by condensing the light from a six-inch quartz mercury arc by means of a large glass condenser. The tube and the liquid inside are heated by means of a specially constructed electric furnace. The temperature of the liquid is measured with a thermometer dipped into the liquid through an opening in the upper side of the tube. The furnace is calibrated prior to the experiment and the different current strengths required to keep the temperature of the liquid constant at different stages, are determined. The slit of the spectrograph is made wide enough, so that, the image includes also that part of the orientation scattering which separates out as rotational wings.

The same exposure is given at different temperatures without altering the other arrangements. A set of intensity marks is recorded on the plate by the method of varying slit widths. The intensity of the incident light has been kept constant by feeding the mercury arc from a 220-volt battery. In the present investigation, benzene, acetic acid, formic acid and nitrobenzene have been studied. All measurements in the first three cases refer to λ 4358 whereas in nitrobenzene they refer to λ 5460. The density-log intensity curves have been obtained in the usual way for each plate by running the plate through a Moll microphotometer and the relative intensities of the scattering at different temperatures are obtained from these curves. In each one of the cases, three different plates have been obtained and the results given in the following tables represent the mean values of the different sets of readings.

3. Results.

In the last column of Tables I, II, III and IV, the intensities observed at different temperatures are given. The figures are only relative and have no absolute significance. In the first three cases, data regarding the refractive index, compressibility and depolarisation at different temperatures have also been given, so far as available. Compressibility data are taken from *International Critical Tables*, Vol. III for all liquids.

The depolarisation values for benzene, nitrobenzene and acetic acid are taken respectively from Sundara Rama Rao (1936), Ramachandra Rao (1927) and Krishnan (1936). Refractive indices have all been obtained from the recent work of Sundara Rama Rao (1936). In such cases where data are not available at the required temperatures, the temperature variation graphs are drawn and the values deduced therefrom.

TABLE I.

Benzene.†

Temp. ° C.	Refractive index	Compressibility	Depolarisation %	Intensity calculated	Intensity observed
30	1·4950	102·0	38·9	10·00	10·00
49	1·4884	110·0	37·4	10·42	10·47
50	1·4820	119·0	36·3	10·82	11·15
60	1·4752	121·0	34·8	11·14	11·68
70	....	....	....	....	12·09

TABLE II.

Nitrobenzene.‡

Temp. ° C.	Refractive index	Compressibility	Depolarisation %	Intensity calculated	Intensity observed
30	1·54720	52·0	69·0	12·88	12·88
40	1·54173	55·0	68·0	12·48	12·02
50	1·53796	56·5	66·0	11·19	11·75
60	1·53361	59·0	63·0	9·76	11·51
70	....	....	....	..	11·44
80	....	....	....	....	11·15
90	....	....	....	....	11·02
100	....	....	....	....	10·78
110	....	....	....	....	10·42
120	....	....	....	..	9·77

† The results obtained are in good agreement with those reported earlier by Ramachandra Rao.

‡ The results obtained in this case are not in agreement with those reported earlier by Ramachandra Rao.

TABLE III. *Acetic Acid.*§

Temp. ° C.	Refractive index	Compressibility	Depolarisation %	Intensity calculated	Intensity observed
30	1·36963	97·0	47·8	13·80	13·80
40	1·36680	104·0	44·1	13·19	14·17
50	1·36343	111·0	40·8	12·49	14·39
60	1·35958	119·0	38·0	12·14	14·79
70	1·35532	128·0	35·1	11·65	14·58
80	....	....	....	....	14·85
90	....	....	....	....	15·10
100	....	....	....	....	15·72

TABLE IV. *Formic Acid.*¶

Temperature ° C.	Depolarisation %	Intensity observed
30	47·5	16·60
40	44·7	15·31
50	41·8	14·32
60	38·8	14·29
70	36·0	....
80	33·0	13·96
90	30·0	13·80

§ The results obtained in this case are not in agreement with those reported by Krishnan.

¶ Krishnan has also reported a set of diminishing intensities with rise in temperature in this case.

A knowledge of these figures will enable us to calculate the intensity of the scattered light that is to be expected at different temperatures from the following relation (Raman and Krishnan, 1928).

$$I = I_0 \frac{\pi^2}{2d^2} \cdot \frac{RT\beta}{N\lambda^4} (\mu^2 - 1)^2 \frac{6 + 6r}{6 - 7r}$$

where I = Intensity of scattered light; I_0 = Incident light; d = distance of the scattering centre from the point of observation; μ = refractive index of the liquid; r = depolarisation; T = Absolute temperature; β = Compressibility; R = Gas constant; and λ = the wave-length.

The values so calculated for benzene, nitrobenzene and acetic acid are shown in column 5 of their respective tables. These figures are also relative and have no absolute significance.

The compressibility data are not available for formic acid and hence similar calculations could not be made in this case. The depolarisation factors at different temperatures (Krishnan, 1936) are however included in Table IV as they will be referred to later.

4. Discussion of Results.

In the case of benzene, the calculated values and experimental values closely agree with each other. In nitrobenzene, both the calculated and experimental values decrease with rise in temperature but the calculated values decrease more rapidly than the experimental values. In the case of formic acid the intensity as observed experimentally decreases with rise in temperature. For acetic acid, while the observations show that the intensity of scattered light increases with rise in temperature, theoretical calculations show that it decreases with rise in temperature.

The observed results regarding the intensity variation are represented graphically in Fig. 1. The scale chosen does not give any indication of

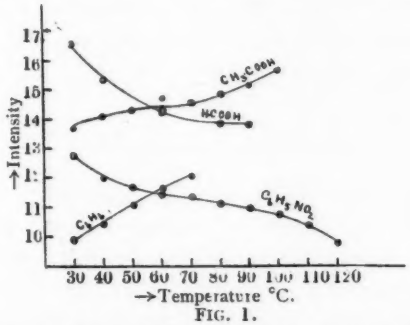

FIG. 1.

the relative scattering powers of the various liquids but is significant only as regards the variation of intensity of the light scattered by any particular

liquid with temperature. The results are somewhat puzzling at first sight as the intensity in benzene and acetic acid increases whereas in formic acid and nitrobenzene, it decreases with increasing temperature. A better insight is obtained into this phenomenon if we separate out the observed aggregate intensity into its constituent parts, namely, the density scattering and the orientation scattering in each case. If we denote the x-component by $2I_x$ and the z-component by $I_z + I_x$ when incident unpolarised light of given intensity is used, then we have (Raman and Krishnan, 1928) :

$$r = \frac{2Ix}{I_z + I_x} = \frac{2n_0 F}{\frac{RT\beta}{N}\left(\frac{\mu^2 - 1}{4\pi}\right)^2 + \frac{7}{3} n_0 F}.$$

It will be seen from the figures given in Tables I to IV that the depolarisation r and the aggregate intensity of scattering are known at a variety of temperatures and hence we can easily evaluate separately the two portions which constitute the aggregate. The results are shown in Table V.

TABLE V.

Temperature °C.	Benzene			Nitrobenzene			Acetic acid			Formic acid		
	Aggregate	Density	Orientation	Aggregate	Density	Orientation	Aggregate	Density	Orientation	Aggregate	Density	Orientation
30	10·00	3·93	6·07	12·88	1·48	11·40	13·80	4·13	9·67	16·6	5·02	11·58
40	10·77	4·41	6·36	12·02	1·48	10·54	14·17	4·78	9·39	15·31	5·07	10·24
50	11·15	4·72	6·43	11·75	1·62	10·13	14·31	5·35	9·04	14·32	5·18	9·14
60	11·68	5·15	6·53	11·51	1·87	9·64	14·79	5·97	8·82	14·29	5·77	8·52
70	..	..		11·44	2·29	9·15	14·58	6·37	8·21	..	..	..
80	..	..		11·15	4·25	6·90	..	..	..	13·96	6·46	7·54
90	..	..		..	..	..	..	..	..	13·80	6·90	6·90

The most significant result that is evident from Table V is the fact that in all cases studied, the density scattering steadily increases with increasing temperature. This is in perfect accord with what we should expect. The orientation scattering on the other hand increases with increasing temperature in benzene and diminishes with increasing temperature in nitrobenzene, formic acid and acetic acid. Benzene should be regarded as a normal case and is characterised by the fact that the density

as well as the orientation scattering and therefore the aggregate increase with rise in temperature. The other three liquids, which are associating, are abnormal in that while the density scattering increases as it should, the orientation scattering diminishes thus indicating a decrease in the optical anisotropy of the scattering unit with increase in the temperature. These two counteracting influences may result either in an aggregate increase as in the case of acetic acid or an aggregate decrease as in the cases of nitrobenzene and formic acid. Thus, we may conclude that in liquids studied, as the variations in the density scattering are quite normal in all cases, the differences in the behaviour of the different liquids are to be attributed to the abnormal behaviour of the orientation scattering.

5. *Summary.*

The intensity of scattering is found to increase with rise in temperature in benzene and acetic acid and to decrease with rise in temperature in nitrobenzene and formic acid. Such differences in the behaviour of these liquids are only apparent and are attributed to the fact that the scattered beam is ordinarily an admixture of two types, namely, density scattering and orientation scattering. When the aggregate intensity is suitably separated into these two constituent parts, the density scattering is always found to increase with increasing temperature as should be expected whereas the orientation scattering sometimes increases (example is benzene) and sometimes decreases (examples are nitrobenzene, acetic acid and formic acid). The observed effect is an aggregate of these two phenomena.

The author takes it his great pleasure to express his most grateful thanks to Mr. S. Bhagavantam, the Head of the Physics Department for the very keen interest he has taken in his work and the valuable guidance he has rendered.

REFERENCES.

Krishnan, R. S. .. .. *Proc. Ind. Acad. Sci.*, 1936, **3**, 126.

Ramachandra Rao, S. .. *Ind. Jour. Phy.*, 1927, **3**, 1.

Raman, C. V. and Krishnan, K. S. .. .. *Phil. Mag.*, 1928, **5**, 498.

Sundara Rama Rao, B. .. *Proc. Ind. Acad. Sci.*, 1936, **3**.

REFRACTIVITY AND MAGNETIC BIREFRINGENCE OF LIQUID MIXTURES.

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1. Introduction.

Studies in magnetic birefringence in mixtures of organic liquids made by Cotton and Mouton (1913), Szivessy (1928) and Chinchalkar (1932) have revealed some interesting features. These authors have found consistently that the observed values do not agree generally with those obtained by calculation with the aid of Langevin's theory. On the basis of the observed results, mixtures could be divided into two classes according as the curves representing the variation of magnetic double-refraction with concentration were either concave or convex towards the axis of concentration compared with the curves drawn on the basis of Langevin's theory.

No satisfactory attempt has been made by any of the above authors to explain these deviations. Chinchalkar alone has given a qualitative description of the phenomena in relation to the variation of magnetic birefringence and optical anisotropy with temperature. He has, however, not attempted to explain these deviations quantitatively.

The present investigation was first undertaken mainly with a view to explain quantitatively the data obtained by Chinchalkar on the magnetic birefringence of liquid mixtures. It may be pointed out here that Chinchalkar made use of Lorentz's additivity relation for determining the refractive index and an analogous relation for the magnetic birefringence in calculating the values of the Cotton-Mouton constant expected for a mixture of a particular concentration. This procedure is open to criticism in both respects as the existence of an anisotropic optical polarisation field is not taken account of either in computing the refractive index or the magnetic birefringence of the mixture. It is felt therefore that the method of calculation should be revised by inserting the observed refractive indices for liquid mixtures in place of the calculated ones and at the same time by making use of the expression for the magnetic birefringence of mixtures derived earlier by the author, which takes into account the anisotropy of the optical polarisation field. With this purpose in view, the refractivity

of a large number of liquid mixtures has been examined at different concentrations and the results in some cases which serve to illustrate the main points in the present investigation are contained in the following pages.

Incidentally it became necessary to examine the data of the refractivity of mixtures by themselves in order to see how far they deviate from Lorentz's law of additivity and how far such deviations are explicable on the basis of an anisotropic polarisation field. From this point of view, Narasimhaiah (1934) already examined the data in the case of two mixtures and came to the conclusion that the observed values are in agreement with Raman and Krishnan's theory.

The author's examination of his own results on the refractivity of the number of mixtures he studied, however, revealed that while the deviations of the observed values from Lorentz's law point to an anisotropic polarisation field, they could not be explained by assuming that the anisotropy of the polarisation field is independent of concentration. Consequently, instead of trying to explain the observed deviations in the refractivity on the basis of Raman and Krishnan's theory, the observed refractivities are made use of in calculating the constants of the anisotropic polarisation field at various concentrations. By inserting the constants so calculated in the modified expression for the Cotton-Mouton constant of a liquid mixture, the observed deviations in the latter could satisfactorily be explained. This procedure, besides explaining for the first time quantitatively the experimental results on the magnetic birefringence of liquid mixtures, furnishes evidence in favour of the view that the anisotropy of the polarisation field in mixtures varies with concentration.

2. *Refractivity of Liquid Mixtures.*

The choice of the liquid mixtures was guided by the list of mixtures already examined by Chinchalkar for magnetic birefringence.

An Abbe refractometer was employed to find the refractive indices of the mixtures at various concentrations. The temperature of the mixture was maintained constant by circulating water through the jackets enclosing the prisms and is noted against each of the mixtures in the following tables. The observed values along with the values calculated on the basis of Lorentz's equation, namely,

$$\frac{n^2-1}{n^2+2}=\frac{v_1}{v_1+v_2}\times\frac{n_1^2-1}{n_1^2+2}+\frac{v_2}{v_1+v_2}\times\frac{n_2^2-1}{n_2^2+2}$$

are given in Tables I to VII. In the above equation, n stands for the refractive index of the mixture of components of refractive indices n_1 and n_2 and volumes v_1 and v_2 respectively in a total volume (v_1+v_2) of the mixture.

In all the mixtures studied, it has been observed that the total volume is merely the sum of the volumes of the constituents.

TABLE I.

Benzene – CCl_4 mixture at 26°·8 C.
Refractive index of CCl_4 = 1.4562
,, of Benzene = 1.4960

Volume of Benzene in 6 c.c. of the mixture	5 c.c.	4 c.c.	3 c.c.	2 c.c.	1 c.c.
n Observed ..	1·4902	1·4844	1·4775	1·4709	1·4639
n Lorentz's theory ..	1·4885	1·4820	1·4750	1·4690	1·4626
n Raman and Krishnan theory	1·4894	1·4829	1·4762	1·4696	1·4629

TABLE II.

Toluene – CCl_4 mixture at 28°.2 C.
Refractive index of CCl_4 = 1.4554
,, of Toluene = 1.4917

Volume of Toluene in 6 c.c. of the mixture	5 c.c.	4 c.c.	3 c.c.	2 c.c.	1 c.c.
n Observed ..	1·4869	1·4803	1·4751	1·4688	1·4621
n Lorentz's theory ..	1·4855	1·4795	1·4734	1·4674	1·4614

TABLE III.

Nitrobenzene – CCl_4 mixture at 28°.5 C.
Refractive index of Nitrobenzene = 1.5478
,, of CCl_4 = 1.4552

Volume of Nitrobenzene in 6 c.c. of the mixture	5 c.c.	4 c.c.	3 c.c.	2 c.c.	1 c.c.
n Observed ..	1·5344	1·5212	1·5053	1·4887	1·4724
n Lorentz's theory ..	1·5319	1·5162	1·5007	1·4853	1·4702

TABLE IV.

CS_2 – CCl_4 mixture at 26°.8 C.
Refractive index of CS_2 = 1.6222
,, of CCl_4 = 1.4562

Volume of CS_2 in 6 c.c. of the mixture	5 c.c.	4 c.c.	3 c.c.	2 c.c.	1 c.c.
n Observed ..	1·5920	1·5622	1·5336	1·5078	1·4820
n Lorentz's theory ..	1·5929	1·5642	1·5365	1·5092	1·4824
n Raman and Krishnan theory	1·5929	1·5649	1·5372	1·5099	1·4829

TABLE V.

CS_2 – Benzene mixture at 26°.8 C.
Refractive index of CS_2 = 1.6222
,, of Benzene = 1.4960

Volume of Benzene in 6 c.c. of the mixture	5 c.c.	4 c.c.	3 c.c.	2 c.c.	1 c.c.
n Observed ..	1·5144	1·5334	1·5530	1·5750	1·5972
n Lorentz's theory ..	1·5162	1·5367	1·5574	1·5786	1·6001

TABLE VI.

CS_2 – Chlorobenzene mixture at 26°.4 C.
Refractive index of CS_2 = 1.6224
,, of Chlorobenzene = 1.5212

Volume of CS in 6 c.c. of the mixture	5 c.c.	4 c.c.	3 c.c.	2 c.c.	1 c.c.
n Observed ..	1·6030	1·5830	1·5664	1·5500	$1·535_0$
n Lorentz's theory ..	1·6050	1·5878	1·5708	1·5541	$1·537_6$

TABLE VII.

CS_2 — Bromobenzene mixture at 27° C.
Refractive index of Bromobenzene = 1.5560
,, of CS_2 = 1.6222

Volume of CS_2 in 6 c.c. of the mixture	5 c.c.	4 c.c.	3 c.c.	2 c.c.	1 c.c.
n Observed ..	1·6095	1·5974	1·5864	1·5754	1·5650
n Lorentz's theory ..	1·6107	1·5996	1·5886	1·5776	1·5668

The results contained in the above tables are graphically represented in Figs. 1 to 7. Circles represent values obtained on the basis of Lorentz's

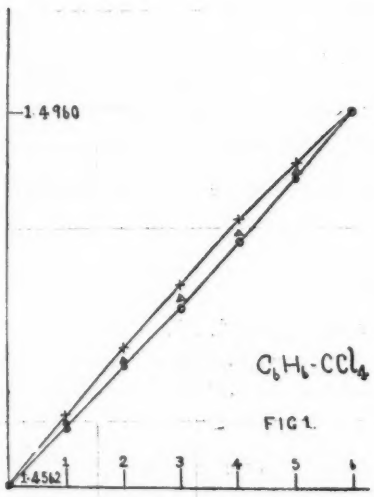


FIG 1.

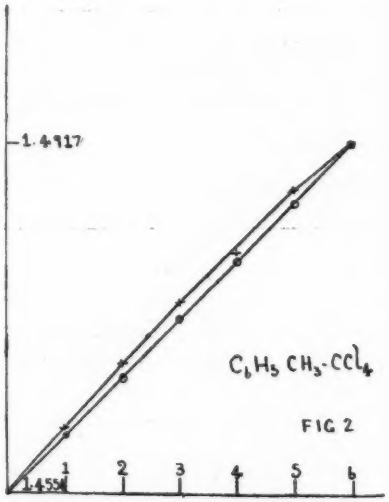


FIG 2

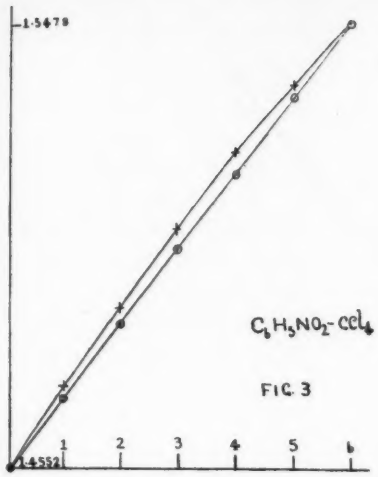


FIG. 3

→Ref. Index

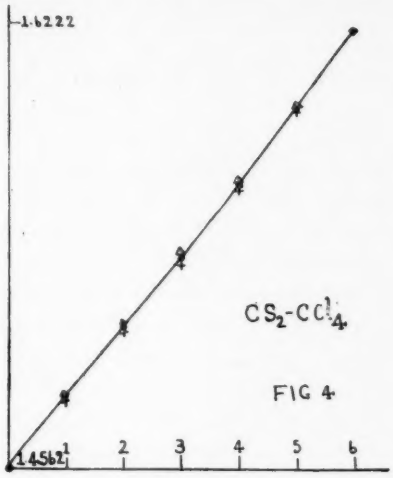


FIG 4

→Ref. Index

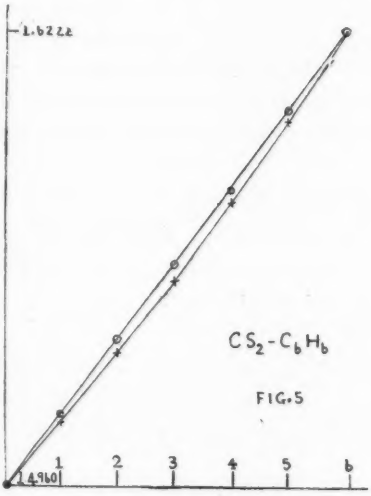


FIG. 5

→Ref. Index

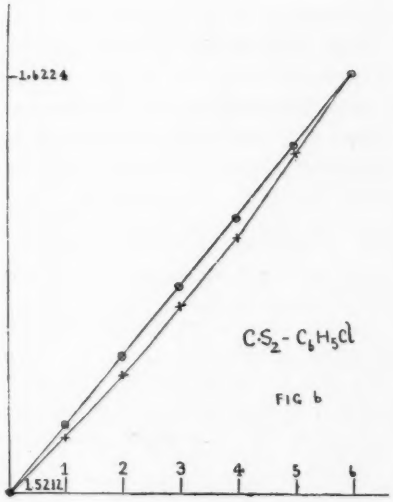
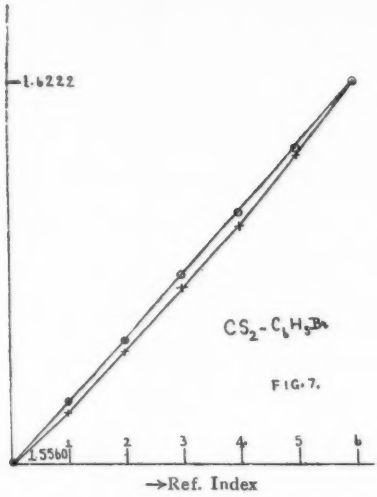


FIG 6

→Ref. Index



theory. Crosses represent the observed values. Triangles represent values obtained on the basis of Raman and Krishnan theory.

A glance at the curves will show in the first place, that there are marked deviations from the Lorentz's law in every case and in the second place that these deviations fall into two classes. In the first three cases we find that the observed values are higher than the values calculated. In the last four cases where CS_2 is the common component for the mixtures, we find that the observed values are less than those calculated on the basis of Lorentz's theory.

3. Modification of Lorentz's Expression.

Applying the idea of the anisotropic polarisation field theory, one obtains the following expression for the refractive index of the mixture

$$\frac{n^2 - 1}{4\pi} = \frac{\nu_1 (B_1 + B_2 + B_3) + \nu_2 (B_1' + B_2' + B_3')}{3}$$

ν_1 and ν_2 being the number of molecules of the respective components in 1 c.c. of the mixture. B's represent the effective optic moments. We may express the refractive index in terms of the gaseous optic moments as follows :

$$\frac{n^2 - 1}{4\pi} = \frac{\nu_1 (b_1 + b_2 + b_3) + \nu_2 (b_1' + b_2' + b_3')}{3 \{1 - \frac{1}{3}\nu_1 (b_1 p_1 + b_2 p_2 + b_3 p_3) - \frac{1}{3}\nu_2 (b_1' p_1' + b_2' p_2' + b_3' p_3')\}}$$

p's represent here the constants of the anisotropic polarisation field. If the molecule of one of the components is optically and geometrically

isotropic (*e.g.*, CCl_4) and if the molecule of the other component be assumed to possess an axis of symmetry,

$$\frac{n^2-1}{4\pi} = \frac{\nu_1 (b_1 + 2b_2) + \nu_2 \cdot 3b'}{3\{1 - \frac{1}{3}\nu_1 (b_1 p_1 + 2b_2 p_2) - \frac{4\pi}{3} \nu_2 b'\}} \quad .. \quad .. \quad (1)$$

To make use of the above equation, one requires to know the values of b_1, b_2, p_1, p_2 and b'. The mode of calculating these from the known values of refractive index of the liquid, δ_v and δ_l, is already indicated in a previous paper by the author (1935). To calculate b' for CCl_4, it is assumed that both the molecule and the polarisation field surrounding the same are isotropic and the Lorentz's formula is applied.

Formula (1) is in the first instance made use of to calculate the refractive indices of mixtures on the assumption that values of p_1 and p_2 derived for a pure liquid in the above manner also represent the coefficients of the anisotropic polarisation field in mixtures irrespective of the concentration of the latter. The two typical cases contained in Tables I and IV will suffice to illustrate the disagreement between the observed values and the values so calculated.

As the results with other mixtures are similar, the calculated values in their case are not reproduced in the tables.

The results of these calculations are also represented graphically in Figs. (1) and (4) which refer to the mixtures in question.

It will be easily noticed from these curves that the introduction of an anisotropic polarisation field with a constant set of p_1 and p_2 does not very much improve the results. There is only a slight improvement in the case of Benzene CCl_4 mixture, whereas in the case of $CS_2 - CCl_4$ mixture, the modified theory led to results which are in greater disagreement with experiment.

These facts are very significant as the cases under investigation conform very closely to the requirements of the theory inasmuch as all the three molecules involved, *viz.*, CS_2, CCl_4 and C_6H_6 are nonpolar and hence non-associating. Further the two mixtures chosen are such that one of the constituents in both cases, *viz.*, CCl_4 is optically isotropic and is surrounded by an isotropic polarisation field whereas the other constituent which is either CS_2 or C_6H_6 possesses an axis of symmetry. In view of this, the agreement observed by Narasimhaiah (1934) in the case of the mixtures whose data he examined by employing a constant set of p_1 and p_2 at different concentrations must, at best, be regarded as fortuitous.

4. Variation of the Coefficients of Anisotropy with Concentration.

Instead of therefore trying to explain the observed refractive indices, it is obviously more fruitful to calculate the values of p_1 and p_2 which will give the observed values of refractive index by making use of equation (1) and the auxiliary equation

$$p_1 + 2p_2 = 4\pi$$

The following tables give the values of p_1 and p_2 so calculated at different concentrations in the case of 3 mixtures.

TABLE VIII.

Benzene—CCl_4 mixture.

Volume of Benzene in 6 c.c. of the mixture	5 c.c.	4 c.c.	3 c.c.	2 c.c.	1 c.c.
$p_1/4\pi$	0·5246	0·5098	0·5081	0·4934	0·4730
$p_2/4\pi$ ..	0·2377	0·2451	0·2460	0·2533	0·2635

TABLE IX.

Toluene–CCl_4 mixture.

Volume of Toluene in 6 c.c. of the mixture	5 c.c.	4 c.c.	3 c.c.	2 c.c.	1 c.c.
$p_1/4\pi$ ..	·5224	·5170	·5022	·4908	·4936
$p_2/4\pi$ ..	·2388	·2415	·2511	·2546	·2532

TABLE X.

CS_2–CCl_4 mixture.

Volume of CS_2 in 6 c.c. of the mixture	5 c.c.	4 c.c.	3 c.c.	2 c.c.	1 c.c.
$p_1/4\pi$ ..	·2542	·2416	·2396	·2282	·2292
$p_2/4\pi$ ..	·3729	·3792	·3802	·3859	·3854

The general case where both the components are anisotropic is more complicated and is hence not dealt with here.

The inference from the above representation is that we can divide the mixtures into two classes. In the former class, of which benzene-CCl_4 is the typical representative, the polarisation field becomes more and more isotropic with diminishing concentration of benzene. In the latter, of which $CS_2 - CCl_4$ is the typical representative, the polarisation field becomes more and more anisotropic with diminishing concentration of CS_2. It is interesting to note here that a similar classification of liquid mixtures is also forthcoming from the observations of Chinchalkar on the magnetic birefringence. Those mixtures in which the polarisation field is becoming more and more isotropic with diminishing concentration of the anisotropic constituent show a magnetic birefringence-concentration curve which is concave towards the concentration axis. The other type, in which the polarisation field is becoming anisotropic with diminishing concentration of the anisotropic constituent, shows a birefringence-concentration curve which is convex towards the concentration axis. This close resemblance has furnished the clue for the proper explanation of the observed deviations in magnetic birefringence and this aspect is dealt with in the following section.

5. *Magnetic Birefringence in Liquid Mixtures.*

In an earlier paper, the author (1929) has derived the following expression for the Cotton-Mouton constant of mixtures taking into account the anisotropic polarisation field.

$$C_M = \frac{1}{20} \times \frac{n_0^2 - 1}{n_0 \lambda K T} \times \frac{\nu_1 [(a_1 - a_2)(B_1 - B_2) + \cdots] + \nu_2 [(a_1' - a_2')(B_1' - B_2') + \cdots]}{\nu_1 (b_1 + b_2 + b_3) + \nu_2 (b_1' + b_2' + b_3')}$$

The letters have the usual significance.

If the molecule of one of the constituents possesses an axis of symmetry (*i.e.*, $b_2 = b_3$; $a_2 = a_3$, etc.) and that of the other is geometrically and optically isotropic, the expression reduces to

$$C_M = \frac{1}{10} \frac{n_0^2 - 1}{n_0 \lambda K T} \times \frac{\nu_1 (a_1 - a_2)(B_1 - B_2)}{\nu_1 (b_1 + 2b_2) + \nu_2 \cdot 3b'}$$

We can express this C_M as a fraction of the C_M of the pure liquid which is the birefringent constituent in the above equation. The C_M of the pure liquid, according to Raman and Krishnan theory, is given by

$$C_M = \frac{1}{10} \times \frac{n_1^2 - 1}{n_1 \lambda K T} \times \frac{(a_1 - a_2)(B_1^* - B_2^*)}{b_1 + 2b_2}$$

Thus the relative birefringence in terms of that of the pure liquid is given by

$$\frac{n_0^2 - 1}{n_0} \times \frac{n_1}{n_1^2 - 1} \times \frac{B_1 - B_2}{B_1^* - B_2^*} \times \frac{(b_1 + 2b_2)}{(b_1 + 2b_2 + \nu_2/\nu_1 \times 3b)} \quad \cdots \quad \cdots \quad (2)$$

It ought to be noted here that the values of B_1 and B_2 in the above equation, *i.e.*, the effective optic moments of the molecule of the birefringent component in solution are different from B_1^* and B_2^*, the effective optic moments of the same in the pure liquid state. They also change with concentration because in the first place, the optical susceptibility of the mixture is different from that of the pure liquid and is changing with concentration and in the second place, the values of p_1 and p_2 which govern their magnitudes as we have seen above also change with concentration.

With this precaution, values of the relative birefringence in the case of three mixtures, as shown below, are calculated and shown along with the values calculated on the basis of a formula used by Chinchalkar and derived earlier by Bergohlm (1917), Szivessy (1921). The latter is as follows and is derivable from equation (2) by putting $p_1 = p_2 = \frac{4\pi}{3}$

$$\text{Relative } C_M = \frac{v_1}{v_1 + v_2} \times \frac{n_1}{(n_1^2 + 2)^2} \times \frac{(n_0^2 + 2)^2}{n_0}$$

Chinchalkar, in his calculations, made use of n_0 derived from Lorentz's additivity relation and as such similar procedure has been adopted in calculating the values in column 3 of the following tables. This would mean that so far as the values in column 3 are concerned, the anisotropy of the optical polarisation field has not been taken account of either in computing the refractive index or the Cotton-Mouton constant. On the other hand, values in column 2, are derived from the observed refractivities and on the basis of the author's expression for C_M which takes into account the anisotropy of the optical polarisation field.

TABLE XI.

Benzene–CCl_4 mixture.

Partial volume of Benzene ..	0·833	0·667	0·500	0·333	0·167
Rel. birefringence calculated (author) ..	0·862	0·724	0·547	0·380	0·200
Rel. birefringence calculated (Chinchalkar) ..	0·829	0·660	0·492	0·327	0·163

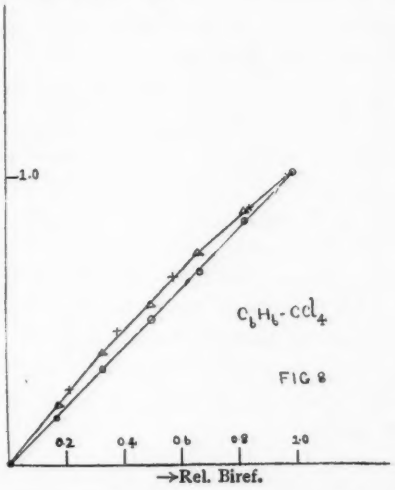
TABLE XII. *Toluene–CCl_4 mixture.*

Partial volume of Toluene ..	0·832	0·667	0·500	0·333	0·167
Rel. birefringence Calc. (author)	0·843	0·688	0·542	0·369	0·184
Rel. birefringence Calc. (Chinchalkar) ..	0·809	0·645	0·481	0·319	0·159

TABLE XIII. *CS_2–CCl_4 mixture.*

Partial volume of CS_2 ..	0·833	0·667	0·500	0·333	0·167
Rel. birefringence Calc. (author)	0·685	0·525	0·387	0·251	0·126
Rel. birefringence Calc. (Chinchalkar) ..	0·814	0·637	0·468	0·306	0·150

The above values are calculated for the concentrations at which the refractivities have been measured. It may be noted that these concentrations are somewhat different from those employed by Chinchalkar. Such a difference does not however matter as the results are ultimately represented graphically in Figs. 8 to 10.*



* In these figures, crosses represent observed values, circles represent values obtained on the basis of Chinchalkar's expression and triangles represent values obtained on the basis of author's expression.

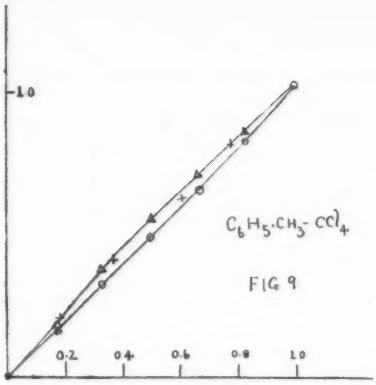


FIG 9

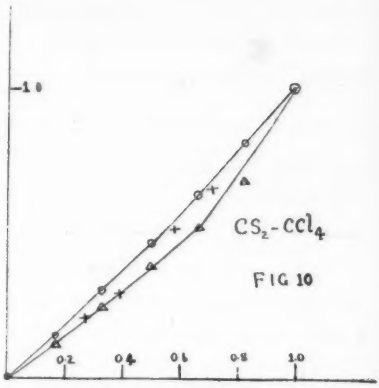


FIG 10

The agreement between the values calculated according to the author's expression and the observed ones in the case of benzene-CCl_4 and toluene-CCl_4 mixtures is excellent. In the case of CS_2-CCl_4 mixture, two of the observations lie on the author's theoretical curve while the other two lie away from it. Even here the agreement can be regarded as fair, as in the first place, the character of the observational curve, is satisfactorily brought out by the theory employed by the author and in the second place good agreement is found between two of the observed results and the corresponding theoretical results. As the other points are somewhat erratic, they may be due to experimental error.

There is one case, however, *viz.*, nitrobenzene CCl_4 mixture which has not come within the scheme of the explanation offered in the present investigation. The magnetic birefringence-concentration curve of this mixture is convex towards the axis of concentration, while the refractivity curve is concave. The latter, according to the view put forward in this paper, ought to result in the magnetic birefringence curve also being concave, if the magnetic characters of the molecule remain unchanged in solution. From the anomaly observed here, we have, therefore, to suppose that in the case of nitrobenzene the magnetic characters of the molecule also are affected by mixing it with another component, besides the optical characters. Such an assumption is not quite out of place as nitrobenzene is ordinarily an associated liquid.

6. *Summary.*

The two outstanding features which Chinchalkar and other workers have observed in the study of the magnetic birefringence of liquid mixtures have been explained for the first time quantitatively by introducing the

new idea of a varying set of anisotropic polarisation field coefficients. The actual variations which the coefficients undergo with changing concentration have been determined from the observed refractivities of mixtures of the requisite composition. Although only typical mixtures have been dealt with in detail in the course of this paper, it may be remarked that the general conclusions hold good in all the mixtures so far studied.

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REFERENCES.

Bergohlm	..	.. *Archiv. f. Mat. Astr and Fys.*, 1917, **12**, No. 3.
Chinchalkar, S. W.		.. *Ind. Jour. Phys.*, 1932, **7**, 491.
Cotton and Mouton		.. *Compt. Rend.*, 1913, **156**, 1456.
„	..	.. *Ann. Chim. Phys.*, 1913, **30**, 321.
Narasimhaiah	..	.. *Proc. Ind. Acad. Sci.*, 1934, **1**, 34.
Ramanadham, M.	..	.. *Ind. Jour. Phys.*, 1929, **4**, 109.
„	..	.. *Proc. Ind. Acad. Sci.*, 1935, **1**, 281.
Szivessy	..	.. *Zeit. f. Phys.*, 1921, **7**, 285.
Szivessy and Richartz		.. *Ann. der Phys.*, 1928, **86**, 393.

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